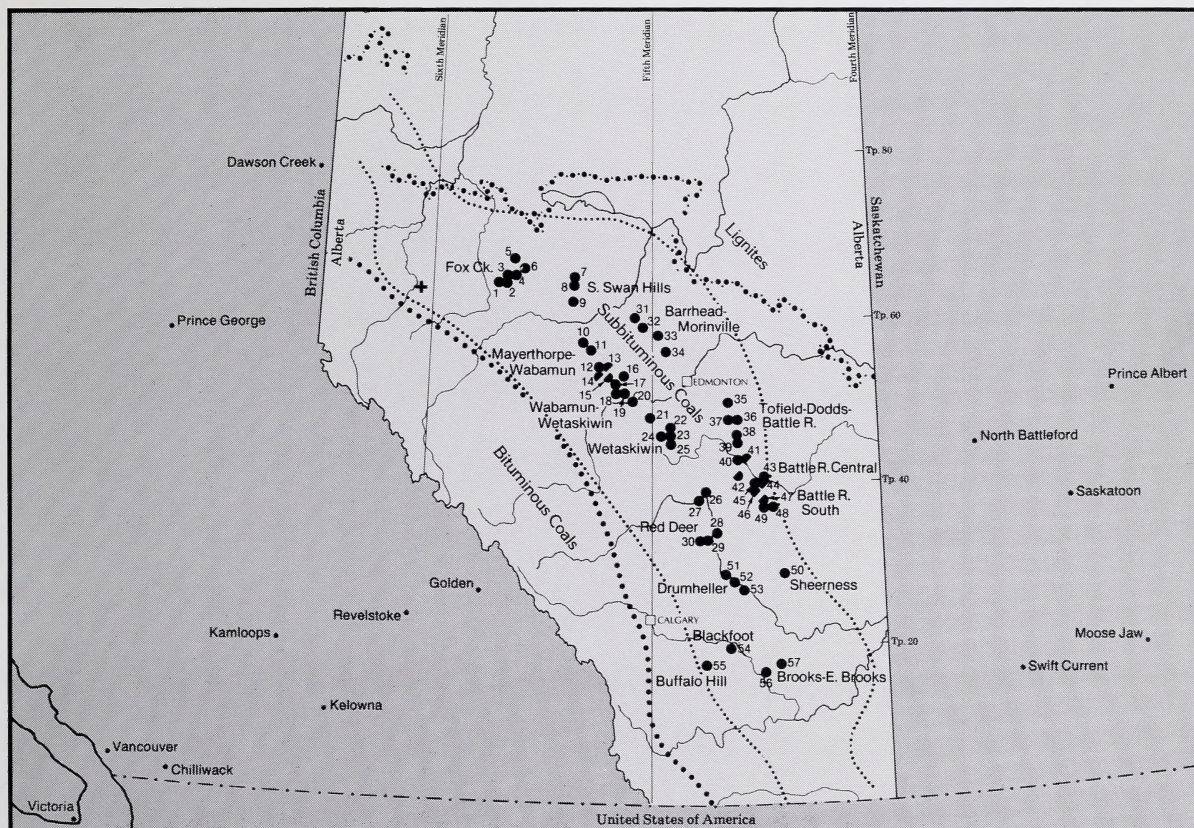


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# Evaluation of Alberta plains coals for pyrolysis and liquefaction processes

S.K. Chakrabartty, M.P. du Plessis



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S.K. Chakrabartty, M.P. du Plessis

|           |  |     |
|-----------|--|-----|
| Table 1   | Chemical composition of coals          | 1   |
| Table 2   | Physical properties of coals           | 2   |
| Table 3   | Proximate analysis of coals            | 3   |
| Table 4   | Ultimate analysis of coals             | 4   |
| Table 5   | Calorific value of coals               | 5   |
| Table 6   | Swelling index of coals                | 6   |
| Table 7   | Proportion of volatile matter in coals | 7   |
| Table 8   | Proportion of fixed carbon in coals    | 8   |
| Table 9   | Proportion of ash in coals             | 9   |
| Table 10  | Proportion of moisture in coals        | 10  |
| Table 11  | Proportion of volatile matter in coals | 11  |
| Table 12  | Proportion of fixed carbon in coals    | 12  |
| Table 13  | Proportion of ash in coals             | 13  |
| Table 14  | Proportion of moisture in coals        | 14  |
| Table 15  | Proportion of volatile matter in coals | 15  |
| Table 16  | Proportion of fixed carbon in coals    | 16  |
| Table 17  | Proportion of ash in coals             | 17  |
| Table 18  | Proportion of moisture in coals        | 18  |
| Table 19  | Proportion of volatile matter in coals | 19  |
| Table 20  | Proportion of fixed carbon in coals    | 20  |
| Table 21  | Proportion of ash in coals             | 21  |
| Table 22  | Proportion of moisture in coals        | 22  |
| Table 23  | Proportion of volatile matter in coals | 23  |
| Table 24  | Proportion of fixed carbon in coals    | 24  |
| Table 25  | Proportion of ash in coals             | 25  |
| Table 26  | Proportion of moisture in coals        | 26  |
| Table 27  | Proportion of volatile matter in coals | 27  |
| Table 28  | Proportion of fixed carbon in coals    | 28  |
| Table 29  | Proportion of ash in coals             | 29  |
| Table 30  | Proportion of moisture in coals        | 30  |
| Table 31  | Proportion of volatile matter in coals | 31  |
| Table 32  | Proportion of fixed carbon in coals    | 32  |
| Table 33  | Proportion of ash in coals             | 33  |
| Table 34  | Proportion of moisture in coals        | 34  |
| Table 35  | Proportion of volatile matter in coals | 35  |
| Table 36  | Proportion of fixed carbon in coals    | 36  |
| Table 37  | Proportion of ash in coals             | 37  |
| Table 38  | Proportion of moisture in coals        | 38  |
| Table 39  | Proportion of volatile matter in coals | 39  |
| Table 40  | Proportion of fixed carbon in coals    | 40  |
| Table 41  | Proportion of ash in coals             | 41  |
| Table 42  | Proportion of moisture in coals        | 42  |
| Table 43  | Proportion of volatile matter in coals | 43  |
| Table 44  | Proportion of fixed carbon in coals    | 44  |
| Table 45  | Proportion of ash in coals             | 45  |
| Table 46  | Proportion of moisture in coals        | 46  |
| Table 47  | Proportion of volatile matter in coals | 47  |
| Table 48  | Proportion of fixed carbon in coals    | 48  |
| Table 49  | Proportion of ash in coals             | 49  |
| Table 50  | Proportion of moisture in coals        | 50  |
| Table 51  | Proportion of volatile matter in coals | 51  |
| Table 52  | Proportion of fixed carbon in coals    | 52  |
| Table 53  | Proportion of ash in coals             | 53  |
| Table 54  | Proportion of moisture in coals        | 54  |
| Table 55  | Proportion of volatile matter in coals | 55  |
| Table 56  | Proportion of fixed carbon in coals    | 56  |
| Table 57  | Proportion of ash in coals             | 57  |
| Table 58  | Proportion of moisture in coals        | 58  |
| Table 59  | Proportion of volatile matter in coals | 59  |
| Table 60  | Proportion of fixed carbon in coals    | 60  |
| Table 61  | Proportion of ash in coals             | 61  |
| Table 62  | Proportion of moisture in coals        | 62  |
| Table 63  | Proportion of volatile matter in coals | 63  |
| Table 64  | Proportion of fixed carbon in coals    | 64  |
| Table 65  | Proportion of ash in coals             | 65  |
| Table 66  | Proportion of moisture in coals        | 66  |
| Table 67  | Proportion of volatile matter in coals | 67  |
| Table 68  | Proportion of fixed carbon in coals    | 68  |
| Table 69  | Proportion of ash in coals             | 69  |
| Table 70  | Proportion of moisture in coals        | 70  |
| Table 71  | Proportion of volatile matter in coals | 71  |
| Table 72  | Proportion of fixed carbon in coals    | 72  |
| Table 73  | Proportion of ash in coals             | 73  |
| Table 74  | Proportion of moisture in coals        | 74  |
| Table 75  | Proportion of volatile matter in coals | 75  |
| Table 76  | Proportion of fixed carbon in coals    | 76  |
| Table 77  | Proportion of ash in coals             | 77  |
| Table 78  | Proportion of moisture in coals        | 78  |
| Table 79  | Proportion of volatile matter in coals | 79  |
| Table 80  | Proportion of fixed carbon in coals    | 80  |
| Table 81  | Proportion of ash in coals             | 81  |
| Table 82  | Proportion of moisture in coals        | 82  |
| Table 83  | Proportion of volatile matter in coals | 83  |
| Table 84  | Proportion of fixed carbon in coals    | 84  |
| Table 85  | Proportion of ash in coals             | 85  |
| Table 86  | Proportion of moisture in coals        | 86  |
| Table 87  | Proportion of volatile matter in coals | 87  |
| Table 88  | Proportion of fixed carbon in coals    | 88  |
| Table 89  | Proportion of ash in coals             | 89  |
| Table 90  | Proportion of moisture in coals        | 90  |
| Table 91  | Proportion of volatile matter in coals | 91  |
| Table 92  | Proportion of fixed carbon in coals    | 92  |
| Table 93  | Proportion of ash in coals             | 93  |
| Table 94  | Proportion of moisture in coals        | 94  |
| Table 95  | Proportion of volatile matter in coals | 95  |
| Table 96  | Proportion of fixed carbon in coals    | 96  |
| Table 97  | Proportion of ash in coals             | 97  |
| Table 98  | Proportion of moisture in coals        | 98  |
| Table 99  | Proportion of volatile matter in coals | 99  |
| Table 100 | Proportion of fixed carbon in coals    | 100 |

Cover:  
Map showing location of  
various coal deposits in  
Alberta plains region.

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# Table of contents

|  |    |
|--|----|
| Abstract   | 1  |
| Introduction   | 1  |
| Test coals   | 2  |
| Experimental procedures                              | 3  |
| Pyrolysis experiments                                | 3  |
| Liquefaction experiments                             | 3  |
| Pyrolysis results                                    | 4  |
| Liquefaction results                                 | 5  |
| Conversion-liquid yield                              | 5  |
| Discussion   | 6  |
| Coal characteristics and processes                   | 6  |
| Pyrolysis behavior                                   | 6  |
| Liquefaction behavior                                | 8  |
| Liquefaction reaction model                          | 9  |
| Coal characteristics and susceptibility to processes | 10 |
| Conclusions  | 12 |
| References   | 22 |

## Tables

|           |  |    |
|-----------|--|----|
| Table 1.  | The proximate and elemental analysis of reference samples from Alberta plains coal deposits    | 13 |
| Table 2.  | Chemical compositional variations  | 13 |
| Table 3.  | Variation in functional groups   | 14 |
| Table 4.  | Physical structural variations   | 14 |
| Table 5.  | Variation in maceral compositions  | 14 |
| Table 6.  | Major and minor elements in the inorganic constituents of test coals                           | 15 |
| Table 7.  | Properties of the solvents used in the evaluation tests  | 15 |
| Table 8.  | Liquefaction test procedures   | 15 |
| Table 9.  | Comparison between Fischer assay and modified assay by TGA                                     | 16 |
| Table 10. | Particle size effect in TGA micro-assay  | 16 |
| Table 11. | Pyrolysis product distribution: projected and experimental                                     | 16 |
| Table 12. | Fischer gas analysis   | 17 |
| Table 13. | Proximate and elemental analysis (ASTM) of 550-Fischer char                                    | 17 |
| Table 14. | Conversion values for liquefaction processes   | 18 |
| Table 15. | Liquid yields from liquefaction processes  | 18 |
| Table 16. | Net liquid yields based on blank run normalization   | 18 |
| Table 17. | Computed versus experimental volatile matter content of the test coals                         | 19 |
| Table 18. | Liquefaction conversion and removal of coal-oxygen as CO, CO <sub>2</sub> and H <sub>2</sub> O | 19 |
| Table 19. | Computed potential hydrocarbon source (PHS) matter in test coals                               | 19 |
| Table 20. | Computed yield of distillable products from test coals   | 20 |
| Table 21. | Computed yield of nondistillable products from test coals                                      | 20 |
| Table 22. | Computed soluble product yields from test coals  | 20 |
| Table 23. | Ratio of total extract yield to PHS  | 21 |
| Table 24. | Comparison of Japanese and Alberta Research Council coal liquefaction results                  | 21 |

## Figures

|            |   |    |
|------------|---|----|
| Figure 1.  | Specimen location and stratigraphic model                           | 2  |
| Figure 2.  | Computational diagram: coal structure and pyrolysis products        | 7  |
| Figure 3.  | Extent of deoxygenation versus liquefaction conversion/PHS yield    | 8  |
| Figure 4.  | Huminite reflectance versus conversion                              | 10 |
| Figure 5.  | Pyrolytic yields versus relative molecular size                     | 11 |
| Figure 6.  | Liquefaction conversion yields versus relative molecular size       | 11 |
| Figure 7.  | Conversion yields versus relative aromaticity                       | 11 |
| Figure 8.  | Pyrolysis yields versus relative oxidation state of F <sub>CH</sub> | 12 |
| Figure 9.  | Pyrolysis product distribution                                      | 12 |
| Figure 10. | Liquefaction product distribution                                   | 12 |

## Appendices

|            |  |    |
|------------|--|----|
| Appendix A | Comparative pyrolysis characteristics of other Canadian coals of cretaceous and carboniferous deposits | 23 |
| Appendix B | Comparative liquefaction characteristics of Alberta mountain and foothills coals                       | 23 |
| Appendix C | Definition of some special terms   | 23 |





## Abstract

As a part of the long range coal research program to promote and guide coal-base technology in Alberta and elsewhere, a project of Alberta plains coals evaluation was initiated in 1981 under the sponsorship of the Alberta/Canada Energy Resources Research Fund. The project aims to establish methods of reliable laboratory assays to select and develop process conditions best suited to specific coal regions, and to select coal feedstocks best suited to specific processes. This report summarizes the results of a detailed data analysis obtained from this systematic experimental investigation.

Eleven coal specimens were included for this report, representing central Alberta coal deposits from the basin north to south and east to west of four major coal formations. These are subbituminous Cretaceous coals with an average analysis of 75 percent carbon, 4.5 percent hydrogen, 1 percent nitrogen, 0.5 percent sulfur and 19 percent oxygen, with mean vitrinite reflectance varying from 0.40 to 0.52. The investigation identified selective coal characteristics showing trend-setting behavior in process reactions. Pyrolysis and solvolytic liquefaction reactions were studied as process variations.

Pyrolysis behavior was determined by TGA micro-assays and detailed product analysis using the ISO-approved Fischer-Schrader assay method. Liquefaction tests were conducted in standard one-litre stirred autoclaves.

The empirical molecular weight of coal, the fraction of hydrocarbon-yielding volatile products, the oxidation state of the volatile carbon structure, the mean vitrinite reflectance, and the molecular fragment representing potential hydrocarbon source matter (PHS) in solvolytic liquefaction showed trend-setting effects in pyrolysis and liquefaction reactions. In-

dividual coals within this set differed mainly in molecular sizes and the orientation of C-H structure.

Pyrolysis of Alberta plains coals produced abundant low-boiling hydrocarbons not reported by standard assay techniques. The mean pyrolytic conversion to low temperature 550°C char was 72 percent ( $\pm 3$  percent), allowing 13.5 wt. percent ( $\pm 3$  percent) coal conversion to distillable oil and tar by products. Normally, the Fischer liquid yields reported for these coals are around 5 to 7 wt. percent of dry, ash-free (daf) coal.

Although the depositional history of coal was found to influence the solvolytic liquefaction behavior, each specimen showed a variable degree of conversion or product distribution, in both solvolysis and pyrolysis reactions. This investigation confirmed the heterogeneity of coal deposits.

The mean solvolytic conversion for all coals under various process modes was 84 percent ( $\pm 8.0$  percent). The conversion data varied from 79 percent to 95 percent, giving the ranking order in terms of reflectance, extent of deoxygenation reactions and abundance of potential hydrocarbon source matter.

These small-scale experiments conducted at Alberta Research Council laboratories have proved useful not only as screening studies to guide more detailed experimentation with continuous flow process development units, but also by providing insight into the molecular structure of Alberta subbituminous coals. This investigation presents a revised interpretation of coal structure and its physical and chemical behavior, assisting future development of low-severity pyrolysis and liquefaction processes.

## Introduction

Coal is a generic term for geologically restored reserves of solid fossil fuels which are often more dissimilar than alike. Studies have indicated behavioral differences between Carboniferous and Cretaceous coals. Berkowitz *et al.* (1974) and Alberta Research Council researchers observed the low fluidity and high oxygen functionality of western hvb coals compared with highly fluid Carboniferous hvb and mvb coals. Flash heating Carboniferous coals to about 400°C generates much chloroform-soluble matter, whereas the western Canadian counterpart of this rank yields very little. The granular micrinite and semifusinite of western Canadian lvb and mvb coals behave as reactive macerals to impart coke stability (Nandi and Montgomery, 1967, 1972). Similar, and other, observations made for bituminous coals do not necessarily apply to subbituminous coals, but investigation has been minimal. Alberta plains coals are mostly subbituminous and Cretaceous.

Alberta coal measures underly at least 26 percent of the total area of the province, of which about 86,400 square miles are in the plains region. Mineable coal is found in two major stratigraphic horizons, namely, Lower Cretaceous, restricted to the mountain region, and Upper Cretaceous and Lower Tertiary to be found in both the foothills and plains regions. According to Dr. Campbell (1981), Plains coals range in rank from hv-C-bituminous to lignite A, decreasing with distance

from the mountains. By far the largest percentage of mineable reserves are subbituminous C, B or A. Three major plains coaly zones are Oldman, Edmonton (Horseshoe Canyon) and Paskapoo. A fourth coaly zone, Lower Cretaceous in age, underlies the plains at great depth, outcropping only in the far northeast of the province near the Athabasca oil sands deposits. As a part of the long range coal research program, evaluation of this valuable resource was initiated with the objectives of promoting and guiding future development of coal-base technology in Alberta and elsewhere.

In any coal utilization process (combustion, gasification or liquefaction), the thermal fragmentation of coal structure generates very fragile but fluid molecules. This key reaction determines the ultimate yield of useful products. Because of coal's unknown structure and heterogeneity, exact description of its thermochemistry is difficult. Currently there is no reliable method of predicting pyrolysis behavior from given coal characteristics and process conditions. The challenge is to develop reliable laboratory methods for characterizing coals under simulated pyrolysis conditions and to correlate these "assays" with data from continuous process units (Chakrabarty *et al.*, 1982a).

In solvolytic liquefaction, besides coal thermochemistry, solvents play a cooperative role by swelling and permeating the porous coal particles, by allowing exchange of protons or hydrogen atoms, and by



generating or quenching free radical chemical species forming fluid molecules. These processes lead to increased solubility by inducing extra fluidity in coal fragments. Therefore, features of coal in terms of inherent and induced "fluidity," and of solvents in terms of permeability, strength of solvation, and oxidation-reduction capacity are of primary value requiring special understanding in improving coal liquefaction technology. In early liquefaction studies, Boomer *et al.* (1935) reported exhaustive catalytic hydrogenation of Alberta coals in tetralin and petroleum solvent to

define the maximum conversion of coal to liquid and gaseous products. Few subbituminous coals of the Alberta plains were included in that study (appendix II).

This report summarizes methods of reliable laboratory assays assisting selection of coal feedstocks best suited to specific processes and development of process conditions best suited to specific coal regions. Several results, quoted in this report are expected to represent near-optimum process conditions in batch operations.

## Test coals

For this investigation, 15 "coal regions" were delineated for studies suited to the liquefaction and pyrolysis process industry (Campbell and du Plessis, 1983). These regions consist of 57 "deposits." From 1981 to 1983, the Alberta Research Council Coal Sample Bank collected representative specimens from 11 such deposits as reference samples. These were analyzed for physical and chemical structural properties, elemental and maceral composition, and reactivity characteristics for processing.

The deposits are from four distinct horizons (Obed-Marsh, Scollard member of the Paskapoo, Horseshoe Canyon and Oldman Formations), but are closely spaced in age between 57 and 62 million years.

In the Alberta plains, the ASTM coal rank ranges from high volatile A subbituminous to lignite A; the highest in rank is the deposit along the southwest boundary of the plains near the Rocky Mountain foothills, with rank decreasing at increasing distances eastward and northeastward. Figure 1 describes the location of coal specimens within a geological stratigraphic model, and table 1 gives the composition of the samples studied between 1981 and 1983. All

eleven coals were characterized by their pyrolysis behavior. For liquefaction studies, eight coals were tested by Alberta Research Council researchers and four coals by Japanese researchers. Table 2 indicates that differences in the heating values of these samples are not wide enough to distinguish ranking order. The average weight percentage compositions of moisture ash-free (daf) coal from each location, calculated from the analyses of randomly drawn specimens from over 300 tests, seem to be as follows: carbon at  $75.03 \pm 0.57$  percent, hydrogen at  $4.47 \pm 0.44$  percent, nitrogen at  $1.11 \pm 0.56$  percent, sulfur at  $0.46 \pm 0.15$  percent, and oxygen at  $18.53 \pm 0.92$  percent.

The minor differences in the elemental compositions may be properly judged by atomic ratios of the constituent elements given in table 2. Obed-Marsh and Oldman coals seem close in elemental composition, having identical oxygen, nitrogen and hydrogen content per 100 carbon atoms. There is hardly any variation in composition among samples from Paskapoo deposits, and variation is limited to hydrogen content in Horseshoe Canyon coals.

A structural variation in oxygen functional groups of

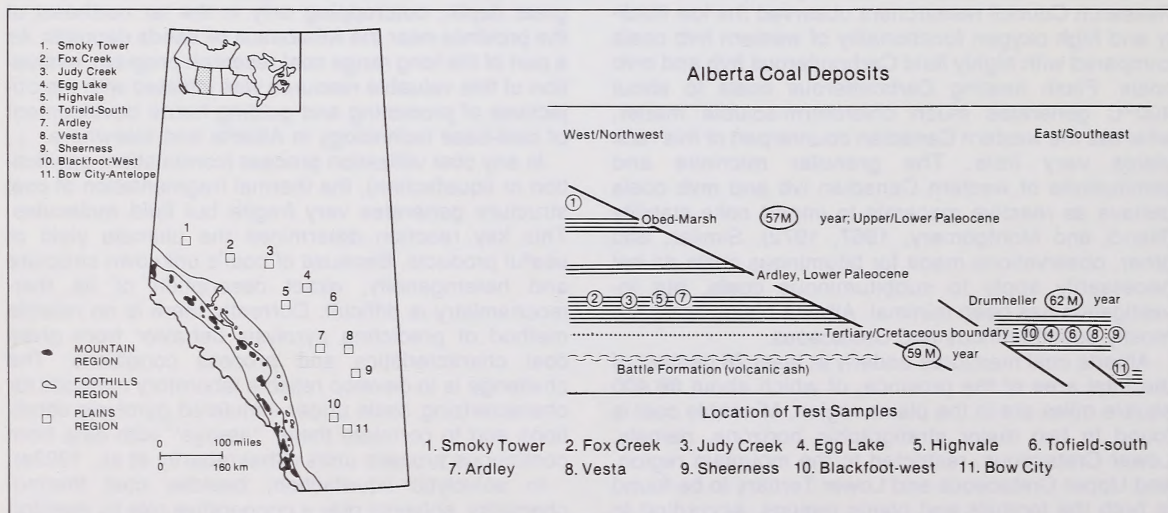


Figure 1. Specimen location and stratigraphic model (not to scale)



the order 1 to 2 meq/g was observed for all 11 samples (table 3). Variations in nitrogen and sulfur functional groups were insignificant. Assuming that aromatic C-H, C-N and C-O functions are preserved in ASTM fixed carbon, "aromaticity" of the individual specimens was calculated (table 4). This aromaticity is lower for the Oldman Formation than for coals from the Cretaceous/Paleocene boundary. The coals from Paskapoo Formation have the highest aromaticity.

The petrographic compositions of all samples were determined independently by S. Parkash at the Alberta Research Council laboratory, and of five samples (coals 1 and 5 to 8) by the Japanese Geological Survey Laboratory (table 5). A 10 percent to 15 percent variance in vitrinite content reported from two different laboratories is not unusual considering the state-of-the-art in subbituminous coal petrography. Moreover, the reliability of "representative" sampling of specimens from the deposits and sample preparation for petrographic analysis is also worth considering. The variance shown in the analyses by two different laboratories is between selected samples from four deposits.

With this analytical limitation, and defining vitrinite content as a reactivity indicator for pyrolysis and liquefaction properties, the Horseshoe Canyon coals were more enriched with reactive macerals than the other three formations. Within Horseshoe Canyon, the Vesta deposit has fewer reactive macerals (though not according to the Japanese analysis). The Oldman deposit ranks second, followed by the Paskapoo and Obed-Marsh deposits.

The other reactive macerals, particularly liptinite, also vary among the coals. Liptinite may be responsible for tar yield in the pyrolysis process (Chakrabarty *et al.*, 1982; du Plessis and Chakrabarty, 1982). Deposits from the Paskapoo Formation, particularly in the Ardley area, showed the highest concentration of liptinite. Obed-Marsh and Horseshoe Canyon coals had comparable liptinite distribution, except for the unusually low value for the Vesta deposit. The Oldman

Formation coals had the least liptinite content.

The huminite random reflectance value (percent  $R_0$ ) presumably represents ranking order or state of coal maturation. The maturation processes depend on age, depth of burial, tectonic pressure due to mountain building, and increase in overburden. The coals from the Oldman and Obed-Marsh Formations showed the highest reflectance, suggesting greater maturation. The Horseshoe Canyon coals are the least mature. Coals from the Paskapoo Formation are of medium rank between the Horseshoe Canyon and Oldman formations, with maturity increasing gradually among the Judy Creek, Fox Creek, Highvale and Ardley deposits (table 4).

The surface areas, densities and porosities of coal particles from each deposit do not show any distinct relationship with ranking order based on reflectance. The capacity moisture (table 1) and random reflectance values (table 4), however, seem to be collinear: coal with high capacity moisture showed low reflectance.

The third criterion of conventional coal properties is emphasized in the literature and relates to quality and disposition of mineral matter. In coal liquefaction studies, the influence of the inorganic matter associated with the feed coal is debatable. Various silicate minerals in this group of coals may act as Lewis acids and influence pyrolysis or liquefaction behavior or both. Pyrite has been claimed to provide a positive catalytic effect on coal pyrolysis products either in situ or in gas phase reaction. Total sulfur content of the test coals is very low (0.5 percent daf). This amount is present mostly as pyrite in a finely divided state, therefore pyrite content of the test coals can be compared. Table 6 gives the distribution of major and minor elements in the inorganic constituents of these test samples. There is very little variation in trace element content among specimens; and of major elements, variation in sodium content for coals 1, 3 and 7 versus coals 5 and 8 is noteworthy.

## Experimental procedures

### Pyrolysis experiments

The ISO-approved Fischer-Schrader assay method was applied to establish the pyrolysis behavior of eleven coals. A packed bed of coal is heated in an aluminum retort from ambient temperature to 550°C at a rate of 6.5 C°/min over 1.5 hours. The water and tar of the volatile products are condensed in a vessel (tar condenser) at ice-bath temperature. Product water is distilled off using benzene or toluene as an azeotropic carrier and tar is weighed after removal of all solvent from the tar condenser. The gas yield is calculated as the difference between weights of the dry input coal and the sum of dry char, product water and tar.

Here, high-resolution gas chromatography determined the gas composition using standard gas mixtures for calibration of peak areas. The char samples

were recovered under helium and analyzed for proximate and elemental studies.

As a simplified procedure of comparing pyrolysis behavior of coal, a programmable thermogravimetric analyzer examined the weight loss of the coal specimens under defined conditions of sample size, particle size, carrier gas flow rate and heating rate. A series of experiments led to a useful micro assay technique which duplicated the Fischer-Schrader assay results.

### Liquefaction experiments

All tests were conducted in a one-litre stainless steel autoclave equipped with a magnetic stirring system and internal cooling coil. A mixture of pulverized (60



U.S. mesh) coal (50 g daf), designated solvent (1 part daf coal, 2.5 parts solvent W/W) and catalyst (1 part daf coal, 0.03 to 0.05 part catalyst W/W) was placed in the metal liner and inserted into the autoclave. The autoclave was then purged with the designated gas, pressurized and heated to the desired temperature. The heating rate varied between 3.5 and 4.5 C°/min and the reaction time was measured from the moment the autoclave reached the reaction temperature. For all tests, a total of three hours was maintained for heating, reacting and cooling, between charging and discharging the autoclave.

Solvents for the various experiments were anthracene oil, hydrogenated anthracene oil, and bitumen (from the Alberta Research Council oil sands sample bank, Suncor deposit). These were presumably enriched in polycondensed aromatics (anthracene oil), polycyclic hydroaromatics (hydroanthracene oil), or substituted polycyclic aliphatics and aromatics (bitumen). Table 7 shows the elemental analysis, boiling point range and arbitrary composition (given as the compound-class-type distribution) of these solvents. The analysis of hydrogenated anthracene oil (used by Japanese researchers) was not available.

Five different process modes, identified as PC-1 through PC-4-2, provided variability in solvent properties, catalysts and reducing atmosphere. Experiments to determine conditions of optimum conversion established the temperature and pressure of test reactions in individual process modes. Table 8 shows typical test conditions for the five types of process mode. Results reported here are for the tests giving near optimum conversion.

The PC-1 process mode used ferric oxide as the catalyst. In the PC-3 mode, water-soluble potassium molybdate was emulsified in the solvent before being charged into the autoclave. In PC-2 processes (PC-2 and PC-4-2), potassium carbonate was the catalyst. The PC-1 mode used hydrogen as the reducing gas, whereas the PC-2 mode used carbon monoxide and steam.

The work-up procedure for the recovery and

characterization of products consisted of:

- analysis of the gaseous products during pressure reduction and cooling of the autoclave;
- atmospheric distillation of the autoclave contents followed by vacuum distillation; and
- extraction of the nondistillable residue with toluene and/or pyridine.

The distillable products are termed naphtha and medium oil. The last fraction (solid, including inorganic mineral and catalyst) is the unconverted residue, the organic part of which is termed "insoluble organic matter" or "IOM".

The conversion factor,  $X$ , was calculated both from the "organic content" of the input coal:

$$X_0 = 100 \times \left(1 - \frac{\text{IOM. gram}}{\text{maf coal [input] gram}}\right)$$

and from ash-closure analysis:

$$X_a = 100 \times \frac{a_r - a_c}{a_r (1 - a_c)}$$

where  $a_c$  = weight fraction of ash (and catalyst) in MF coal, and

$a_r$  = weight fraction of ash (and catalyst) in MF residue

The net conversion,  $X$ , of the moisture ash-free coal to gaseous and liquefiable products is obtained by averaging  $X_0$  and  $X_a$ 's. The difference between  $X_0$  and  $X_a$ 's for test runs giving optimum conversion was between 0.5 percent and 2.2 percent. Thus  $X$  represents the average optimum conversion of coal to gaseous and liquefiable products in a specific process mode for two or more runs under similar conditions.

Pyrolysis reactivity,  $R_{py}$ , is defined as 100 minus 550°C char yield of moisture ash-free coal. It is also a statistical mean of the  $R_{py}$  over several runs (Fischer assay) calculated from the actual weight of char (after correcting for ash content), and the calculated yield from ash closure analysis.

## Pyrolysis results

The "effective volatile content" is a parameter measuring potential liquid and gas yields from a given coal subjected to any pyrolysis process. The cumulative weight loss under isothermal heating, if conducted stepwise over a range of temperatures, is very often different from the ASTM proximate volatile matter content. Rapid heating of pulverized coal particles dispersed in an inert gas, or held in a monolayer of thin bed, often gave volatile yields exceeding proximate volatile contents. An arbitrarily chosen assay technique can characterize pyrolysis behavior of a sample set, as defined by the technique, and within the set relative to each other. This was the rationale of the present study.

From the scouting experiments with the programmable thermogravimetric apparatus (TGA), parametric conditions were ascertained to duplicate Fischer-Schrader results with TGA. Table 9 compares the Fischer-Schrader results with those of the TGA micro assay technique which shows that the quality and composition of chars prepared by two different methods were identical — differences between the volatile matter contents were negligible, and the nitrogen contents (determined for Highvale and Blackfoot chars only) were the same. Thus, heating of these coals to 550°C in a static bed of bulk sample (20 to 30 g) over a long period (6 C°/min for 90 min), or rapid heating (50°/min for 10 to 12 min) of a micro sample (20 to 30 mg), yield-



ed comparable char and volatile materials from disproportionation of the samples. In TGA micro assays, variation in particle size did not affect the disproportionation reactions. Table 10 compares the results of TGA-volatile yields at 400°C and 550°C from coal particles of 200 and 100 to 40 micron sizes.

It is interesting that the "fixed carbon" remaining in 400°C or 550°C chars (64.0 percent and 63.5 percent, respectively) is very close to ASTM fixed carbon of the original coal ( $63.8 \pm 0.85$  percent), indicating that net volatile yields from these coals are independent of particle size and mode of heating. Flash heating or sequential heating to higher temperatures will not increase the yields of volatile products above ASTM volatile matter contents.

The 550°C assay results are given in table 11. The char yields are averages of duplicate macro and micro assays and the volatile product yields (water and tar) are averages of duplicate Fischer assays. After removing water from the tar collector by azeotropic distillation, benzene/toluene was distilled off and the residues were weighed to record "oil plus tar" yields. Some volatile hydrocarbons, ethers, and phenols boiling below 110°C would have been lost and were included as gas yields. From this set of coals, the average char yields (550°C) were  $72.0 \pm 2.8$  percent and tar yields (boiling over 110°) were  $5.11 \pm 2.8$  percent of daf coal.

The Fischer gas was analyzed chromatographically using GC columns with packing material standardized for pyrolysis and refinery gas analyses. Within the limitations of GC analysis, the gas compositions were determined as accurately as possible and are shown in table 12.

The average carbon dioxide (CO<sub>2</sub>) content of the Fischer gas was  $53.4 \pm 6$  percent and the methane content was  $17.9 \pm 3.5$  percent. The variation of

methane and CO<sub>2</sub> within the set is noteworthy. High values of CO<sub>2</sub> were compensated by low values of methane, and vice versa. This relation is not true for comparative yields of carbon monoxide (CO) and methane. High values of combined yields of CO and CO<sub>2</sub>, however, were always reflected by low methane yields; the gas with 76.4 percent CO plus CO<sub>2</sub> would invariably contain 14.4 percent methane, while gas with 66.4 percent CO plus CO<sub>2</sub> would have 21.4 percent methane.

This relation between yields of oxides of carbon and methane suggests that the oxidation state of volatile carbons in this set of coals has a specific distribution pattern — high oxidation states of volatile carbon structures are associated with high yields of carbon oxides, which proportionately depress the methane yields. It would be of interest to know how the disposition of oxygen within the carbon structures influences the cleavage reactions of branched chain, cyclic and aromatic ring carbons. (Further discussion follows under "Liquefaction behavior.")

A general trend of high tar yields from coals with low oxidation states of volatile carbons, and consequently low char yields, was observed but the relative standing of individual coals showed some anomaly. The average compositions of resulting chars from all coals were approximately constant, with daf weight percentage carbon at  $84.2 \pm 0.5$  percent, hydrogen at  $2.9 \pm 0.2$  percent and oxygen at  $10.7 \pm 1.0$  percent (table 13). Only the nitrogen content varies, depending on the coals from which the char is prepared.

The experimental approach of TGA micro assays coupled with detailed analysis of Fischer assay products has provided valuable insight into the differences among subbituminous coals from various regions in the Alberta plains.

## Liquefaction results

### Conversion-liquid yield

The experiments conducted to study the liquefaction properties of these coals can be classified into two groups: (1) hydroliquefaction designated as PC-1, PC-3 and PC-4-1, and (2) solvolytic liquefaction designated as PC-2 and PC-4-2. These tests simulated the process conditions of piloted technology under the titles of the I.G. Farben process (PC-1), improved I.G. Farben process with dispersed catalyst (PC-3), COSTEAM process (PC-2) and innovative process using novel solvent or novel concept (PC-4). The test results were obtained in terms of overall conversion (as weight percentage of daf coal converted to gas, liquid and extracts) and liquid product yields (sum of distillable liquids and extractable matter as a percentage of the solvent impact). A set of data of experimental results was collected on the basis of selected replicated experiments where total mass recovery was more than 90 percent and reaction conditions were

near optimum. The population pool, thus defined, provided a standard deviation of 3.0 percent for conversion and 3.6 percent for liquid yield values. These results are summarized in table 14 for conversion and table 15 for liquefaction yield values.

The average conversion values of coal from Highvale, Ardley, Judy Creek and Fox Creek and Smoky Tower regions range between 78 and 86 percent. Conversion of coals from Egg Lake, Battle River, and Vesta ranges from 93 to 95 percent. The spread between replicated runs is indicative of process sensitivity to variations in coals. PC-3, the improved I.G. Farben process with dispersed catalyst hydroliquefaction, displays the least sensitivity and PC-1, classical catalytic hydroliquefaction, the highest sensitivity. Process sensitivity is more pronounced with Paskapoo coals which are less reactive than the Horseshoe Canyon coals.

The liquid yields calculated as weight percent of in-

put solvent, vary from 112 to 130 percent from Paskapoo coals, and 120 to 131 percent from Horseshoe Canyon coals (table 15). Thus, from the standpoints of both conversion and liquid yields, the entire population pool can be grouped into reactivity groups which coincide with geological formation; the Horseshoe Canyon coal is more reactive than Paskapoo coal and the Smoky Tower (Obad-Marsh Formation) coal has intermediate reactivity.

Since total liquid yields based on input solvent in the above consideration do not reveal how much coal was converted to liquid products, net liquid yields based on blank run normalization were also determined for these coals. The procedure requires analyses of the product

distribution in the tests where all the reactants except coal were allowed to react under the conditions similar to a comparative experiment with coal. The results of such computations are given in table 16. The processes, PC-3 (hydroliquefaction) and PC-2 (solvolytic liquefaction), gave the highest net liquid yields. PC-4-2 was particularly effective for low reactivity coals (Paskapoo Formation) when bitumen was used as solvent. In the novel solvent process, PC-4, carbon monoxide is more effective than hydrogen to generate liquids from coals. Computation on the basis of blank run normalization may not be very reliable if solvent acts as a reactant also.

## Discussion

### Coal characteristics and processes

The efficiency of a process or differences in reactivities of a set of coals in a specified process can be judged if the chemistry and physics of the reactions are well understood. Experiments performed at the Alberta Research Council or at the Japanese laboratories were not geared to address this topic critically. The present study was aimed at finding a pattern of conversion behavior of Alberta plains coals, and provided some significant observations which are discussed below. While trying to develop a "systematics-of-reactivity" pattern and the quality/quantity relationship for liquefaction and pyrolysis product yields, due consideration was given to the difficulties encountered in establishing experimental procedure.

### Pyrolysis behavior

The pyrolysis results (Fischer-Schrader assay) showed that the nonvolatile products (char) obtained through pyrolysis of the ten coal samples are identical in carbon and hydrogen content (table 13). Effects of decomposition and disproportionation reactions of coal particles on the elemental compositions of volatile and nonvolatile products is readily detectable in the product distribution pattern. The oxidation state of the volatile carbons determines the composition of gaseous products and the yield of tar. Of all elements, nitrogen is the least volatile and is preserved in non-volatile char.

Assuming that at least one nitrogen atom is left behind in the solid product of disproportionation of a hypothetical coal molecule, the equivalent weight of the solid products (char) in terms of one nitrogen atom can be calculated readily from analysis of the char. Having established the unit weight of char, other volatile components can be added, to synthesize the original hypothetical coal molecule. For example, from the yields of water, the number of hydroxyl groups are calculated and added to the core structure; the remaining oxygen is assumed to appear as CO and CO<sub>2</sub> and would correspond to -COOH and to -C-O groups in the

original coal. Finally, the unaccounted carbon and hydrogen must be accommodated as volatile hydrocarbons arising from decomposition and disproportionation reactions. Thus, hypothetical unit structures of coals and their pyrolysis product distribution based on the elemental compositions of chars and coals are computed and given in table 11 and figure 2. The computed oil and tar yields, which are two to three times higher than the experimentally determined tar yields should include the missing gaseous hydrocarbons and phenols. The computed gas yield is therefore lowered to a minimum. The distribution of gases as oxides of carbon and C<sub>1</sub>-C<sub>6</sub> hydrocarbon complies with the gas chromatogram of Fischer gas analysis.

The next consideration is the validity of these computational data. The assumptions on which these computations are based are: (1) 550°C char and water yields are correct and reproducible; (2) water is formed from -OH groups; (3) oxides of carbon are generated by decarboxylation and decarbonylation; (4) some organic nitrogen and sulfur are transformed into ammonia and hydrogen sulfide; and (5) all volatile carbon-hydrogen structures evolve as oil and tar along with C<sub>1</sub>-C<sub>6</sub> hydrocarbons. On the basis of these assumptions, the leftover volatile matter in the 550°C char can generate only CO and H<sub>2</sub> during subsequent analysis. The ASTM fixed carbon from these chars would have a composition of CH<sub>0.22</sub>N<sub>0.01</sub>S<sub>0.002</sub>O<sub>0.002</sub>. In earlier work (Howard, 1981) it was demonstrated that the second stage of coal decomposition (600 to 800°C) yielded CO and hydrogen as the main gaseous products.

The origin of volatile matter of coals can thus be identified. Table 17 gives the computed and the experimentally determined volatile matter contents of the test coals for two stage and single stage pyrolysis reactions. The variance between the experimental and computed data lies within the limits of analytical error (1.6 ± 0.8) percent.

This study suggests that between 6 and 10 percent of coal mass is volatilized in light oil products, and the oil plus tar yields reported by Fischer assay are generally low. The report of 12 to 18 percent liquid hydrocarbon yields from flash pyrolysis and flash



| Coal Location<br>& Unit Weight | Coal Unit Structure | Char Unit Structure<br>& Unit Weight | Tar & Oil<br>Unit Weight |
|--------------------------------|---------------------|--------------------------------------|--------------------------|
| SMOKY<br>TOWER<br>944          |                     |                                      |                          |
| FOX<br>CREEK<br>1473           |                     |                                      |                          |
| JUDY<br>CREEK<br>1784          |                     |                                      |                          |
| HIGHVALE<br>1723               |                     |                                      |                          |
| EGG LAKE<br>1086               |                     |                                      |                          |
| ARDLEY<br>1351                 |                     |                                      |                          |
| VESTA<br>980                   |                     |                                      |                          |
| BLACKFOOT<br>Jerry Mine<br>935 |                     |                                      |                          |
| BLACKFOOT<br>west pit<br>793   |                     |                                      |                          |
| BOW CITY<br>776                |                     |                                      |                          |

Figure 2. Computational diagram: Coal structure and pyrolysis products

hydropyrolysis of subbituminous Cretaceous coals seems justified. This analysis produces the following decreasing pyrolysis reactivity order respecting the potential hydrocarbon yields:

High ... Bow City (20.5), Smoky Tower (17.1)  
 Vesta (14.8), Egg Lake (14.0)  
 Fox Creek (14.2), Highvale (13.8)  
 Judy Creek (13.1)  
 Low ... Blackfoot (11.7), Ardley (11.5)

The number in parenthesis represents potential yields of hydrocarbon gases, oil and tar from 100 parts of moisture and ash-free coal materials. This order can be correlated with the depositional history or geology of the sample set.

## Liquefaction behavior

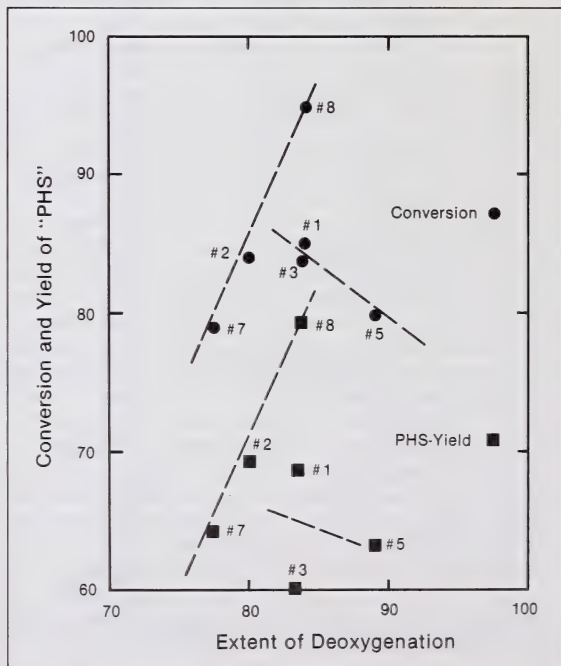
The behavioral differences of the individual Cretaceous subbituminous coals subjected to solvolytic liquefaction can also be related to the depositional history or geology of the set; the sample from Horseshoe Canyon is more reactive than that of Obed-Marsh or Paskapoo. The maturation of the chemical structure (defined by  $R_0$ ), and hence the rank, is also responsible for the variation. In the specimen set, lower ranks have looser chemical structures ( $R_0$  is 0.40 instead of 0.50); consequently the coal is more reactive for solvolytic liquefaction. Coal from Vesta deposits showed the highest reactivity. On this premise, coal 1 (Smoky River) should be least reactive, but its reactivity order placed it between Paskapoo and Horseshoe Canyon coals. This shows that the inherent heterogeneity arising from the depositional history of individual coals has a marked influence also on its reactivity. The ecology of coal 1 is probably different from the others of the set.

Obviously from the elemental analyses, between 18 and 20 percent of the organic mass of this set of coals is oxygen that would appear as waste products in the forms of carbon monoxide, carbon dioxide and water during solubilization and subsequent hydroligneification. This loss of oxygen functions may be associated with the skeletal fragmentation of coal molecules, followed by chemical rearrangement of bonds whose influence on these types of reactions is uncertain.

Table 18 compares the oxygen loss (in the forms of  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) as a statistically derived mean value for each coal subjected to the five liquefaction modes, and to pyrolysis in a static bed up to  $550^\circ\text{C}$  (Fischer assay methods). The thermal cleavage of oxygen functions apparently occurs more extensively in solvolytic liquefaction (77 to 89 percent) than in pyrolysis (56 to 76 percent). The standard deviation of the pyrolysis data indicates the error limit or precision of the analytical method. In contrast, the standard deviations of 4 to 12 percent in solvolytic liquefaction data (computed from several tests using three different solvents and two different reducing atmospheres) represent more than experimental errors and possibly

A trend showing the variation of hydrocarbon gas, oil and tar yields from pyrolysis processes approximately reflects the variation in random reflectance values of huminites (percent  $R_0$ ) in parent coals. Higher rank coals produced higher yields of hydrocarbon. The samples from three deposits — Smoky Tower (Obed-Marsh), Ardley (Paskapoo) and Bow City (Oldman) — with almost the same porosities but different geological origins and maceral compositions, gave hydrocarbon yields in the average proportion 1.5:1.0:2.0. The proportion of reactive to nonreactive macerals of these three coals was 3:2:6. Though the porosities and surface areas do not affect the pyrolytic reactivity of these coals, the rank and composition of the macerals do influence product yields.

reflect the influence of the process modes on oxygen removal. The loss of oxygen during liquefaction is not only higher, but also differs among specimens and process modes. From pyrolysis data, the oxygen in coals 1 and 7 seems more tightly bound than in the other coals; thermal treatment removed 57 percent of oxygen from these two coals, but liquefaction removed 83.5 percent from coal 1 and 77.1 percent from coal 7. Coals 7, 2 and 8 show increased conversion with increased loss of oxygen, but a reverse trend is observed with coals 1, 3 and 5 where higher deoxygenation accompanies lower conversion (figure 3).



**Figure 3.** Extent of deoxygenation versus liquefaction conversion/PHS yield



This relationship between deoxygenation (as CO, CO<sub>2</sub> and H<sub>2</sub>O) and total conversion (to soluble liquid and gas), classifying coals into groups with a positive or negative correspondence, is reflected in the yields of distillable and soluble products. The relationship between PHS (= 100 - CO - CO<sub>2</sub> - H<sub>2</sub>O - IOM) and deoxygenation of the said six coals is also shown in figure 3.

The deoxygenated, intermediate coal fragments are the potential hydrocarbon source (PHS percentage daf coal) and enable evaluation of coal and process types from simple batch autoclave experiments. Table 19 summarizes PHS yields from the set of coals subjected to the various processes (table 8). An average conversion of 84 ± 8 percent was achieved with this set of coals using aromatic, hydroaromatic and naphthenic solvents in an atmosphere of hydrogen or carbon monoxide gas. The average PHS yield from this data set (table 19) is 68 ± 8 percent. Since the difference between total conversion and PHS yield is 16 to 17 wt. percent of daf coal, the PHS still contains 6 to 8 percent oxygen.

Another feature of the solvolytic liquefaction data requires further attention. Tables 20 and 21 show that the computed yield of distillable liquid was not significant except for coal 8 in processes PC-1, PC-3 and PC-4-1. The amount of distillable liquid for coals 2 and 3 was occasionally lower than for the blank run where no coal was used. This is possible only if solvents act as one of the reactants and are transformed into products having different boiling points and other properties. Most of the transformed solvent, after reacting with coal, appears in the soluble products. Table 22, which gives the computed soluble product yields from 100 g of moisture ash-free coal, shows values exceeding 100 g for all tests except for coal 5 subjected to process PC-1. Thus, extractable soluble products from solvolytic liquefaction seem to be derived from both coal and solvent.

The use of multicomponent solvent (for example, anthracene oil or bitumen) makes it almost impossible to isolate and identify solvent-derived products from total

product slurry; and when the solvent becomes a reactant, so-called blank runs with solvent only, are not relevant to product analysis. The only simple alternative is to rely on mass balances to find the contribution of the solvent in liquefaction products and to make a first approximation of the defining reaction routes and product distribution. It was suggested earlier that the distillable and soluble products are derived from PHS in coal. From the ratio of the extract yields (table 23) and PHS of individual coals (table 19), the contribution of the solvent can be quantified. Interestingly, this ratio for the set of coals (table 23) seems constant for each solvent over the entire range of test runs. For anthracene oil and any coal, the ratio is 2.0 ± 0.12, and for bitumen it is 2.5 ± 0.3.

Besides coal reactivity, solvent characteristics may also be responsible for the divergence in conversion data among the processes. PC-1 and PC-3 used anthracene oil, but the catalyst in the latter tests was highly dispersed molybdenum salt. With this change of reactants, conversion increases from 80 to 90 percent. Japanese researchers used hydrogenated anthracene oil and obtained 90 percent conversion with four coals. In PC-3 test runs, dispersed molybdenum catalyst probably transformed anthracene oil into hydrogenated anthracene oil — similar to the solvent used by Japanese researchers. Thus, an undefined mixture of hydroaromatic compounds derived by hydrogenation of anthracene oil provided the highest solvolytic liquefaction of this set of coals. Naphthenic solvent, derived by *in situ* reaction of coal and bitumen (PC-4-1), ranked second in conversion reactivity; and aromatic (anthracene oil) solvent ranked last. This order of effectiveness is derived from test runs with hydrogen as the reducing gas. Experiments conducted with carbon monoxide and steam, however, gave comparable conversion (87 ± 5 percent) in either anthracene oil or bitumen. To achieve this level of conversion with a CO-steam system, basic catalyst (K<sub>2</sub>CO<sub>3</sub>) was necessary. Thus, efficiency of the process modes depends on the solvent and reducing atmosphere used.

## Liquefaction reaction model

These findings from batch autoclave studies on solvolytic liquefaction suggest a simple reaction model:

Coal + Solvent →

[Coal<sub>org</sub>·Solvent]\* + CO + CO<sub>2</sub> + H<sub>2</sub>O + [C<sub>1</sub> - C<sub>4</sub>] gas →  
IOM + Extract + HC (Distillable) + [C<sub>1</sub> - C<sub>8</sub>] gas

The coal and the reacted solvent fragments get locked into a postulated intermediate species (Coal<sub>org</sub>·Solvent)\*, a nondistillable but soluble product, which after 10 to 30 minutes, gradually breaks down to gaseous hydrocarbons (C<sub>1</sub> to C<sub>8</sub>), distillable liquids (HC), and extractable and nonextractable matter. Hydrocarbon gases (C<sub>1</sub> to C<sub>4</sub>), which evolve along with CO and CO<sub>2</sub>, may form pyrolytically from

coal or from coal-solvent intermediate adducts. The role of molecular hydrogen or carbon monoxide in this model is not accounted for.

In the tests conducted by the Japanese researchers, the products were isolated from the product slurry through benzene extraction. The hexane soluble part of the benzene extract was termed "oil" and the insoluble part "asphaltene." In table 24 the combined oil and asphaltene yields, after correcting for solvent contribution in the Japanese process, are compared with the corresponding liquid yields of each coal computed from the Alberta Research Council tests. Recall that in the PC-3 process, anthracene oil should have been hydrogenated to give a reaction comparable to Japanese tests. The compatibility of the data from the two laboratories underscores the reliability of the ex-

perimental results, and hence the reaction model proposed here. These results suggest that the autoclave

test procedure broadly represents a solvolytic type of reaction.

## Coal characteristics and susceptibility to processes

In the preceding sections, coal reactions were analyzed in terms of molecules subjected to physical and chemical environmental effects. Coal, as an organic chemical entity, consists of various molecules containing C, H, N, S and O. Coal characteristics can be defined in relation to the molecular sizes and configurations. To understand chemical transformations in either pyrolysis or solvolytic liquefaction reactions, these "chemical entities" were given an average structure based on the distribution of nitrogen atoms between volatile and nonvolatile fragments. The smallest unit of the "organic chemical entity" surviving as char presumably contains one nitrogen atom. From the elemental analysis of coal and its 550°C char, simple mass-balance calculations establish the ratio of volatile to nonvolatile nitrogen of a coal and provide the structural unit of char (based on a single nitrogen atom) and of the coal from which it forms (figure 2). The definition of molecular size for each coal is then simply the formula weight of an average molecule derived empirically from the elemental composition of coal and its 550°C char containing one nitrogen atom. This molecular size should represent the compositional character of coal, generally referred to by atomic H/C, N/C, S/C and O/C ratios.

The coal molecule contains bonds that are thermally unstable. During heating, these bonds break and new bonds form to give a thermally stable molecule. If this new molecule is a solid, its thermal stability is secured up to the temperature at which it formed. Up to 550°C, part of the carbon evolves as gas, liquid oil, and tar, by breakage of the thermally unstable bonds. Thus, the fraction of carbon ( $f_{CH}$ ) yielding volatile hydrocarbons and oxides of carbons also represents the compositional character of coals. Because of the variation of oxygen content among coals in this volatile portion of molecular structure, the oxidation state of the volatile carbon fragments also characterizes composition. This can be defined as the fraction of oxygen lost in heat treatment of solid carbon structure of coal up to 550°C. From this definition, the  $f_{CH}$  of Horseshoe Canyon coal (Vesta) is the most oxidized and Highvale coal (Paskapoo Formation) is the least.

Another parameter, described earlier as "aromaticity" and derived from the pyrolytic behavior of test samples, may prove significant in characterizing the composition of these coals. It was noted that the parameter  $R_0$ , giving the mean random reflectance of huminite, generally represented rank or stage of maturation. An increase in aromaticity, molecular size, or "compactness" may increase the value of  $R_0$ . Thus, the chemical description of each coal can be based on a hypothetical average molecular size, its physical characteristics, chemical characteristics (such as aromaticity, oxidation state of  $f_{CH}$ , percent

$R_0$ ) and "habitat" within a specific deposit.

The susceptibility of this hypothetical average molecule to process reactions such as pyrolysis, solvolysis, and thermal solvolytic liquefaction can be judged from the yield of thermally stable products or from conversion to such products. Thus, the yields of nonvolatile solids (char in pyrolysis, insoluble organic matter in solvolysis) and of volatile hydrocarbons or distillable liquids (or fragments of coal responsible for generating volatile or distillable liquids) designate the susceptibility of coal to process reactions.

Several illustrations relate the composition characteristics of these coals to their degree of susceptibility to process reactions. A review of data in tables 4, 5 11 and 15 suggests that, for the whole set of coals, the physical properties such as porosity have very little effect on processing behavior. The expected increase in hydrocarbon product due to increased reactive maceral content occurred with three coals: Ardley, Smoky Tower and Bow City. Coals from other deposits (Highvale, Fox Creek, Judy Creek, Vesta and Egg Lake) did not exhibit this increase. It seems that maceral components, by their presence alone, can

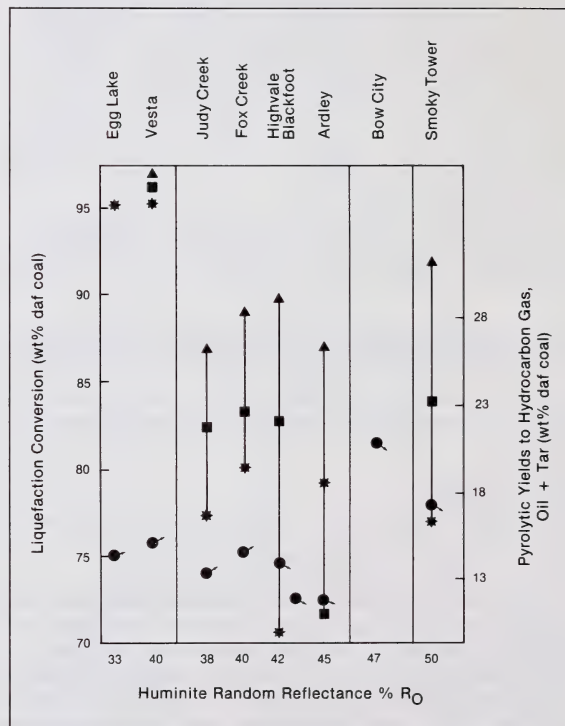


Figure 4. Huminite reflectance versus conversion

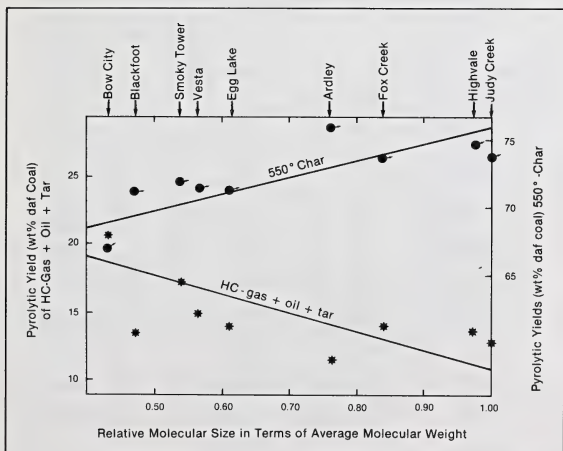


predict some conversion behavior, but not the total yield.

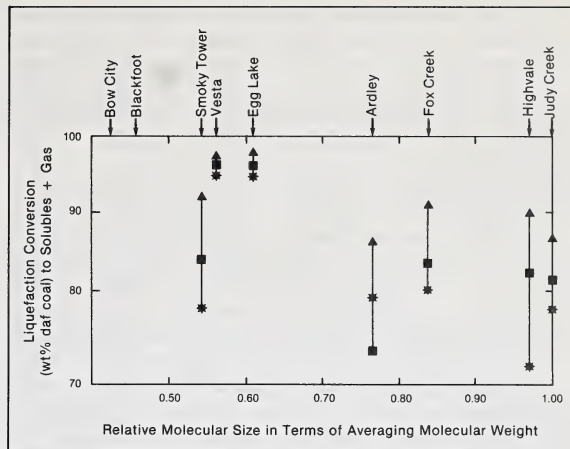
The huminite random reflectance (percent  $R_0$ ) of these coals is quite distinct for each geological formation (figure 4). Horseshoe Canyon coal has the lowest  $R_0$  value and Obed-Marsh has the highest. The values for the Paskapoo and Oldman Formations lie between these two. A general trend of increased pyrolytically generated hydrocarbon yield occurs with increasing  $R_0$  values, but this does not hold for total liquefaction conversion. The highest conversion was obtained with Horseshoe Canyon coal ( $R_0$  33 to 40 percent), followed by Obed-Marsh coal ( $R_0$  50 percent); the conversions of Paskapoo coals ( $R_0$  38 to 45 percent) were the lowest. The Paskapoo coals are of medium rank between those of the Horseshoe Canyon and Oldman Formations. Within the Paskapoo horizon, a gradual increase in maturation occurs among all the deposits — Judy Creek, Fox Creek, Highvale and Ardley. The liquefaction conversion yields of these samples are greatest at the midpoint of the ranking scale (according to percent  $R_0$  values). Thus, the rank of maceral may have greater influence on pyrolytic and solvolytic reactions.

The geological maturation processes ( $R_0$ ) have no bearing on the chemical parameters (like aromaticity or molecular size) of this set of coals. But these coals responded to processing according to certain chemical parameters. Figures 5 and 6 show the relationship between molecular size of individual coals and pyrolysis and liquefaction behavior. With increasing size of the coal molecule, the Fischer char yield increased and hydrocarbon gas, oil and tar yields decreased (figure 5). A similar trend, though not as prominent, was observed in liquefaction reactions (figure 6).

It is known that polycondensed aromatics coke readily and reflectance increases with the extent of aromatic ring condensation. The reflectances of huminites (percent  $R_0$ ) are not related to the molecular



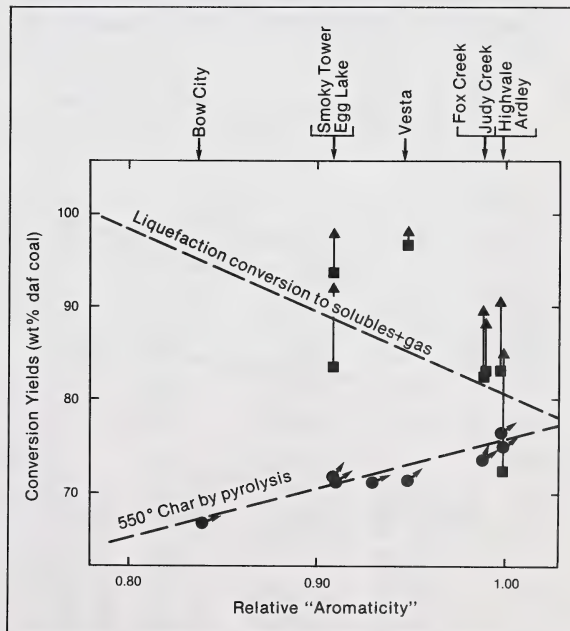
**Figure 5.** Pyrolytic yields versus relative molecular size



**Figure 6.** Liquefaction conversion yields versus relative molecular size

sizes of these coals, and aromaticity is inversely related to percent  $R_0$  values (table 4); yet yields of both Fischer char and insoluble organic matter in liquefaction reactions increased with aromatic content of these coals (figure 7). Consequently, liquefaction conversion values decreased as aromaticity increased. Since this aromaticity is defined in terms of pyrolytic behavior, it represents susceptibility of these coals to coking. Thus, the poor reactivity of Paskapoo coals in liquefaction reactions relates to their coking susceptibility.

These coals have very similar elemental composition (table 2); besides their molecular sizes, the orien-



**Figure 7.** Conversion yields versus relative aromaticity

tation of the elements (especially oxygen) within the molecular framework may induce their individual heterogeneity. In figure 8, the relative oxidation states of the volatile carbon structure ( $f_{CH}$ ) are plotted against pyrolysis product yields and hydrocarbon conversion data. Interestingly, these oxidation states distinguish Paskapoo coals from the rest of the sample-bank coals. Oxygen molecules in Paskapoo coals are present in higher proportions within the non-volatile structure and may be responsible for the ease of coking, leading to a higher yield of char in pyrolysis and IOM in liquefaction reactions. Thus, larger molecules along with a high proportion of oxygen in nonvolatile carbon structures, makes Paskapoo coals less reactive than Horseshoe Canyon or Oldman coals. Since solvents have distinct effects on liquefaction yields as shown by the wide spread in liquefaction data for various coals and process conditions, the reactivity parameters can be manipulated by intelligent application of process modes.

## Conclusions

Eleven coal specimens selected for this investigation were characterized on the basis of coal chemistry. The pyrolysis and liquefaction behaviors of these samples were designated in terms of product distribution under selected reaction conditions. Some of the results are summarized in figures 9 and 10.

These small-scale experiments conducted at Alberta Research Council laboratories have proved useful, not only as screening studies to guide more detailed experimentation of continuous flow process development

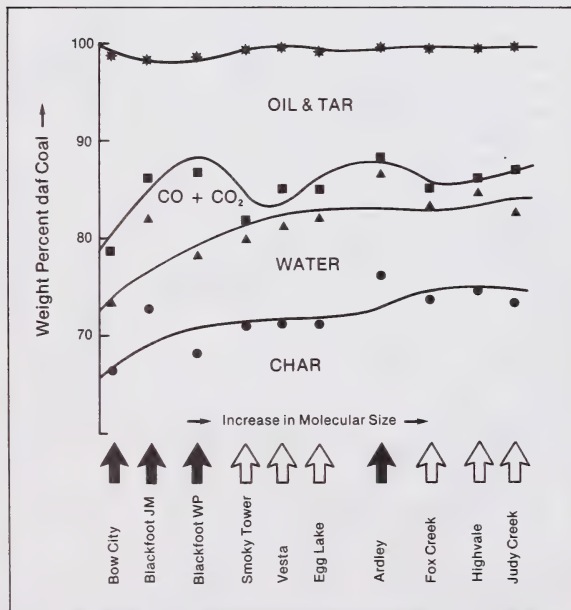


Figure 9. Pyrolysis product distribution

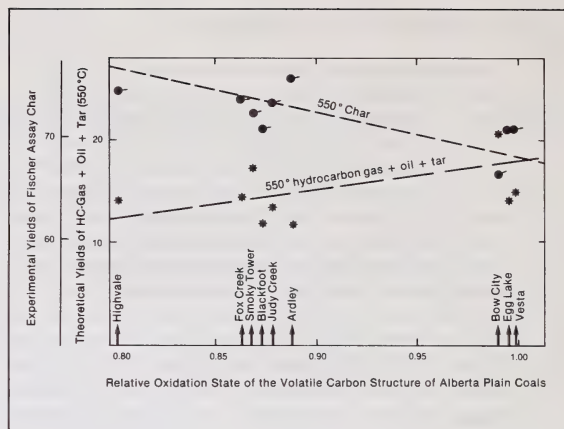


Figure 8. Pyrolysis yield versus relative oxidation state of  $f_{CH}$

units, but also by providing insight into the molecular structure of Alberta subbituminous coals. The work presented here is believed to be a new and useful interpretation of coal structure and its physical and chemical behavior, assisting in future development of low-severity pyrolysis and liquefaction processes.

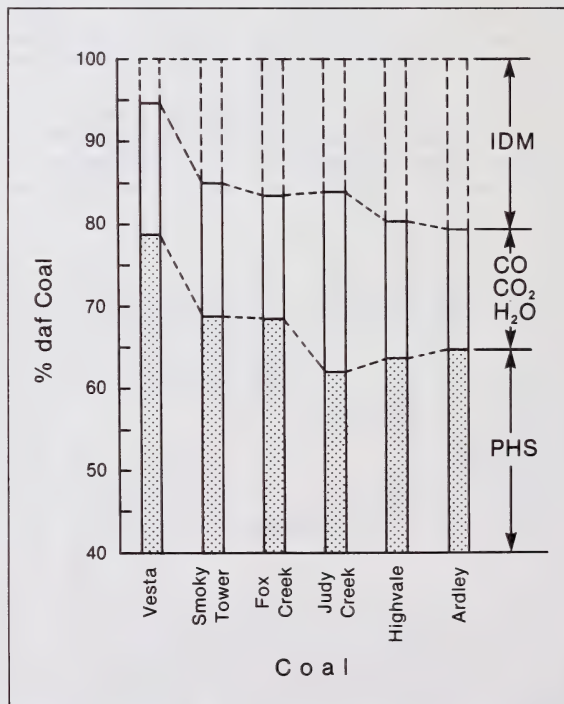


Figure 10. Liquefaction product distribution



**Table 1.** The proximate and the elemental analysis of reference samples of Alberta plains coal deposits (percent)

| Sample specification        |                     |                     |                                |                  |                              |                           |                     |                       |                       |                     |
|-----------------------------|---------------------|---------------------|--------------------------------|------------------|------------------------------|---------------------------|---------------------|-----------------------|-----------------------|---------------------|
| Name                        | Number <sup>1</sup> | Region <sup>2</sup> | Capacity moisture <sup>3</sup> | Ash <sup>4</sup> | Volatile matter <sup>5</sup> | Fixed carbon <sup>5</sup> | Carbon <sup>5</sup> | Hydrogen <sup>5</sup> | Nitrogen <sup>5</sup> | Sulfur <sup>5</sup> |
| Smoky Tower                 | 1                   | -                   | 16.0                           | 20.0             | 43.4                         | 56.5                      | 75.8                | 5.1                   | 1.71                  | 0.54                |
| Fox Creek                   | 2                   | 1                   | 18.6                           | 16.5             | 40.0                         | 60.0                      | 75.8                | 4.2                   | 1.10                  | 0.50                |
| Judy Creek                  | 3                   | 2                   | 19.8                           | 16.0             | 40.5                         | 59.5                      | 75.1                | 4.1                   | 0.87                  | 0.43                |
| Highvale                    | 5                   | 4                   | 19.6                           | 11.4             | 39.6                         | 60.4                      | 75.0                | 4.4                   | 1.08                  | 0.19                |
| Ardley                      | 7                   | 6                   | 19.3                           | 20.0             | 39.3                         | 60.7                      | 75.7                | 4.2                   | 1.17                  | 0.45                |
| Blackfoot                   | 10                  | 13                  | 16.2                           | 19.4             | 43.0                         | 57.0                      | 76.8                | 5.1                   | 1.70                  | 0.80                |
| Blackfoot (JM) <sup>6</sup> | 10a                 | 13                  | 20.2                           | 8.3              | 44.2                         | 55.8                      | 71.5                | 4.1                   | 1.82                  | 0.41                |
| Blackfoot (WP) <sup>7</sup> | 10b                 | 13                  | 19.0                           | 7.0              | 41.3                         | 58.7                      | 74.1                | 4.3                   | 2.00                  | 0.48                |
| Egg Lake                    | 4                   | 7                   | 25.2                           | 14.6             | 43.2                         | 56.8                      | 74.2                | 4.5                   | 1.62                  | 0.42                |
| Tofield                     | 6                   | 8                   | 23.3                           | 24.4             | 43.8                         | 56.2                      | 73.4                | 4.4                   | 1.64                  | 1.20                |
| Vesta                       | 8                   | 9                   | 24.6                           | 12.2             | 41.9                         | 58.1                      | 74.4                | 5.0                   | 1.50                  | 0.63                |
| Sheerness                   | 9                   | 11                  | 25.6                           | 10.9             | 43.2                         | 56.8                      | 73.7                | 4.6                   | 1.68                  | 0.81                |
| Bow City                    | 11                  | 15                  | 15.7                           | 13.7             | 47.1                         | 52.9                      | 75.8                | 5.4                   | 1.83                  | 0.89                |

<sup>1</sup> Sample location number — see figure 1.<sup>2</sup> See Campbell *et al.* (1983), ARC Information Series 101.<sup>3</sup> Weight percentage of wet coal.<sup>4</sup> Weight percentage of moisture-free coal.<sup>5</sup> Weight percentage of moisture ash-free coal.<sup>6</sup> Blackfoot (Jerry mine).<sup>7</sup> Blackfoot (west pit).

Note: Oxygen content = 100 - (C + H + N + S) weight percentage of moisture, ash-free coal.

**Table 2.** Chemical compositional variations

| Sample specification |                  |                              |                     |                       |                       |                     |                     |
|----------------------|------------------|------------------------------|---------------------|-----------------------|-----------------------|---------------------|---------------------|
| Deposit              | Geology          | Calorific value <sup>1</sup> | Carbon <sup>2</sup> | Hydrogen <sup>2</sup> | Nitrogen <sup>2</sup> | Sulfur <sup>2</sup> | Oxygen <sup>2</sup> |
| Smoky Tower          | Obed-Marsh       | 29.8                         | 100                 | 80.1                  | 1.92                  | 0.26                | 16.7                |
| Fox Creek            | Paskapoo         | 29.7                         | 100                 | 66.0                  | 1.24                  | 0.24                | 18.2                |
| Judy Creek           | Paskapoo         | 28.4                         | 100                 | 65.0                  | 1.03                  | 0.21                | 19.4                |
| Highvale             | Paskapoo         | 28.8                         | 100                 | 68.3                  | 1.26                  | 0.10                | 19.4                |
| Ardley               | Paskapoo         | 29.2                         | 100                 | 66.0                  | 1.36                  | 0.22                | 18.7                |
| Blackfoot            | Horseshoe Canyon | 28.7                         | 100                 | 79.1                  | 1.90                  | 0.39                | 15.2                |
| Egg Lake             | Horseshoe Canyon | 28.3                         | 100                 | 72.3                  | 1.80                  | 0.20                | 19.5                |
| Tofield              | Horseshoe Canyon | 27.9                         | 100                 | 71.4                  | 1.90                  | 0.61                | 19.8                |
| Vesta                | Horseshoe Canyon | 29.4                         | 100                 | 80.0                  | 1.73                  | 0.32                | 18.6                |
| Sheerness            | Horseshoe Canyon | 28.1                         | 100                 | 74.4                  | 2.00                  | 0.41                | 19.6                |
| Bow City             | Oldman           | 30.6                         | 100                 | 84.9                  | 2.00                  | 0.44                | 15.9                |

<sup>1</sup> KJ/g daf coal.<sup>2</sup> Elemental analysis expressed as atoms per 100 carbon atoms.

**Table 3.** Variation in functional groups (meq/g daf coal)

| Sample specification |        | Oxygen |       |     |             |       | Nitrogen <sup>1</sup>         | Sulfur <sup>2</sup> |
|----------------------|--------|--------|-------|-----|-------------|-------|-------------------------------|---------------------|
| Name                 | Number | -OH    | -COOH | -O- | Unaccounted | Total | = N-, = NH-, -NH <sub>2</sub> | = S-, -SH           |
| Smoky Tower          | 1      | 5.0    | 0.3   | 4.8 | 0.4         | 10.5  | 0.16                          | 0.07                |
| Fox Creek            | 2      | 5.4    | 0.8   | 5.3 | 0.0         | 11.5  | 0.15                          | 0.07                |
| Judy Creek           | 3      | 4.8    | 1.0   | 5.5 | 0.9         | 12.2  | 0.06                          | 0.05                |
| Highvale             | 5      | 5.4    | 0.5   | 6.0 | 0.3         | 12.2  | 0.18                          | 0.02                |
| Ardley               | 7      | 5.7    | 0.4   | 5.1 | 0.3         | 11.5  | 0.10                          | 0.06                |
| Blackfoot            | 10     | 3.3    | 1.8   | 4.6 | 0.0         | 9.7   | 0.02                          | 0.07                |
| Egg Lake             | 4      | 6.0    | 0.8   | 4.6 | 0.6         | 12.0  | 0.20                          | 0.06                |
| Vesta                | 8      | 5.5    | 0.9   | 4.3 | 0.8         | 11.5  | 0.05                          | 0.09                |
| Bow City             | 11     | 3.8    | 1.2   | 3.9 | 1.1         | 10.0  | 0.03                          | 0.13                |

<sup>1</sup> estimated from the Fischer assay yields of ammonia.<sup>2</sup> estimated from the Fischer assay yields of hydrogen sulfide.**Table 4.** Physical Structure Variations

| Sample specification |        | Relative aromaticity <sup>1</sup> | Huminite <sup>2</sup> percent R <sub>O</sub> | N <sub>2</sub> -surface area <sup>3</sup> | He-density <sup>4</sup> | Porosity <sup>5</sup> percent |
|----------------------|--------|-----------------------------------|--|---|-------------------------|-------------------------------|
| Name                 | Number |                                   |  |   |                         |                               |
| Smoky Tower          | 1      | 0.68                              | 0.49   | 8.8                                       | 1.426                   | 19.1                          |
| Fox Creek            | 2      | 0.74                              | 0.40   | 7.7                                       | 1.467                   | 10.3                          |
| Judy Creek           | 3      | 0.74                              | 0.38   | 11.1                                      | 1.468                   | 20.9                          |
| Highvale             | 5      | 0.75                              | 0.43   | 3.6                                       | 1.449                   | 9.5                           |
| Blackfoot            | 10     | 0.68                              | 0.43   | 3.5                                       | 1.435                   | 22.3                          |
| Egg Lake             | 4      | 0.70                              | 0.33   | 5.7                                       | 1.468                   | 13.6                          |
| Tofield              | 6      | 0.70                              | 0.39   | 9.8                                       | 1.445                   | 13.0                          |
| Vesta                | 8      | 0.71                              | 0.40   | 3.2                                       | 1.417                   | 12.4                          |
| Sheerness            | 9      | 0.70                              | 0.42   | 3.3                                       | 1.407                   | 18.6                          |
| Bow City             | 11     | 0.63                              | 0.46   | 1.3                                       | 1.372                   | 19.4                          |

<sup>1</sup> defined as fraction of total carbon in 850°C fixed carbon.<sup>2</sup> random reflectance percentage of moisture ash-free coal-huminite.<sup>3</sup> m<sup>2</sup>/g daf coal.<sup>4</sup> g/mL daf coal.<sup>5</sup>  $100 \times (1 - d_{Hg}/d_{He})$  where  $d_{Hg}$  = mercury-density and  $d_{He}$  = helium-density.**Table 5.** Variation in maceral compositions (percent volume of mineral matter free coal)

| Coal name   | Huminite(H) | Liptinite(L) | Semifusinite(SF) | Inertinite(I) | (H + L)/(I + SF) |
|-------------|-------------|--------------|------------------|---------------|------------------|
| Smoky Tower | 70.0 (81.6) | 6.4          | 8.6              | 15.0          | 3.24             |
| Fox Creek   | 82.6        | 1.5          | 9.5              | 6.4           | 5.29             |
| Judy Creek  | 72.4        | 5.3          | 8.1              | 14.2          | 3.48             |
| Highvale    | 74.6 (64.8) | 2.1          | 22.2             | 1.1           | 3.29             |
| Ardley      | 59.5 (73.5) | 9.0          | 18.9             | 12.6          | 2.17             |
| Blackfoot   | 91.4        | 1.7          | 1.7              | 5.2           | 13.50            |
| Egg Lake    | 92.4        | 4.2          | 0.8              | 2.6           | 28.41            |
| Tofield     | 92.0        | 4.0          | 2.0              | 2.0           | 24.00            |
| Vesta       | 73.3 (95.1) | 0.3          | 8.9              | 17.5          | 2.79             |
| Sheerness   | 92.7        | 5.3          | 1.2              | 0.8           | 49.00            |
| Bow City    | 82.9        | 3.4          | 3.7              | 10.0          | 6.30             |

Note: Parenthetical reference is analysis reported from the Japanese laboratory which differed from ARC analysis.



**Table 6.** Major and minor elements in the inorganic constituents of test coals (ppm dry wt.)

| Coal No. | Ba   | Na   | Ca    | K    | Mg   | Mn  | Al    | Fe   | Ti  | Sr  | P    | Si    | S    |
|----------|------|------|-------|------|------|-----|-------|------|-----|-----|------|-------|------|
| 1        | 1131 | 519  | 11341 | 1241 | 1417 | 75  | 17894 | 4455 | 629 | 164 | 1025 | 57352 | 4240 |
| 3        | 238  | 447  | 15572 | 501  | 1166 | 151 | 16759 | 3003 | 713 | 135 | 39   | 49256 | 3612 |
| 5        | 488  | 1886 | 15893 | 339  | 842  | 79  | 13570 | 3747 | 402 | 202 | 25   | 23328 | 1786 |
| 7        | 795  | 716  | 16306 | 817  | 1711 | 105 | 19377 | 3928 | 602 | 326 | 1103 | 54760 | 3605 |
| 8        | 688  | 4723 | 8915  | 740  | 943  | 32  | 26987 | 4501 | 444 | 232 | 108  | 34259 | 5538 |
|          | Co   | Cr   | Cu    | Ga   | Li   | Mo  | Ni    | Pb   | Rb  | Sn  | V    | Zn    |      |
| 1        | 20   | 20   | 54    | 20   | 38   | 25  | 36    | 27   | 34  | —   | 65   | 276   |      |
| 5        | 22   | 20   | 52    | 20   | 48   | 20  | 46    | 56   | 27  | 5   | 56   | 197   |      |
| 7        | 20   | 6    | 60    | 25   | 53   | 20  | 28    | 46   | 15  | 8   | 40   | 178   |      |
| 8        | 19   | 25   | 40    | 25   | 52   | 25  | 60    | 37   | 17  | 5   | 23   | 110   |      |

**Table 7.** Properties of the solvents used in the tests

|                          | Anthracene oil         | Alberta bitumen        |
|--------------------------|------------------------|------------------------|
| Initial boiling point    | 204°C                  | 185°C                  |
| Boiling point final      | 520°C                  | >550°C                 |
| Percent aromatic carbon  | 96                     | 32                     |
| Percent carbon content   | 92.5                   | 83.2                   |
| Percent hydrogen content | 5.3                    | 10.7                   |
| Percent nitrogen content | 1.2                    | 0.7                    |
| Percent oxygen content   | 0.5                    | 0.6                    |
| Percent sulfur content   | 0.6                    | 4.8                    |
| Atomic H/C               | 0.69                   | 1.54                   |
| Atomic O/C               | 4.1 x 10 <sup>-3</sup> | 5.4 x 10 <sup>-3</sup> |
| Compound class-type*     |                        |                        |
| Percent hydrocarbons     | 59.4                   | 29.3                   |
| Percent resins           | 32.1                   | 48.2                   |
| Percent asphaltenes      | 8.5                    | 22.5                   |

\* defined in terms of a mobility on thin-layer plates of silica when eluted with a specific solvent system.

**Table 8.** Procedure for liquefaction tests

| Process mode | Reactants   | Rx time (min) | Temperature (°C) | Pressure (MPa) |
|--------------|---|---------------|------------------|----------------|
| PC-1         | Coal, anthracene oil, H <sub>2</sub> gas, ferric oxide                      | 0-45          | 430-470          | 10.5           |
| PC-1 (Japan) | Coal, hydrogenated anthracene oil, H <sub>2</sub> gas, sulfur, ferric oxide | 30            | 430-470          | 10.5           |
| PC-3         | Coal, anthracene oil, H <sub>2</sub> gas, dispersed molybdenum catalyst     | 30            | 430              | 10.5           |
| PC-4(1)      | Coal, Alberta bitumen, H <sub>2</sub> gas, ferric oxide                     | 60            | 400              | 10.5           |
| PC-4(2)      | Coal, Alberta bitumen, CO gas, water, potassium carbonate                   | 60            | 400              | 7.0            |
| PC-2         | Coal, anthracene oil, CO gas, water, potassium carbonate                    | 30            | 400              | 7.0            |

**Table 9.** Comparison of fischer assay data with modified pyrolysis assay by TGA (g/100 g daf coal)

| Coal                        | Fischer assay |                   |                      | Modified pyrolysis assay |                   |                      |
|-----------------------------|---------------|-------------------|----------------------|--------------------------|-------------------|----------------------|
|                             | Char yield    | Char fixed carbon | Char volatile matter | Char yield               | Char fixed carbon | Char volatile matter |
| Ardley                      | 75.1          | 80.7              | 19.3                 | 75.9                     | 80.4              | 19.6                 |
| Highvale                    | 74.5          | 79.6              | 20.4                 | 74.7                     | 81.2              | 18.8                 |
| Fox Creek                   | 74.7          | 81.2              | 18.8                 | 73.8                     | 81.5              | 18.5                 |
| Judy Creek                  | 74.6          | 80.7              | 19.3                 | 73.3                     | 77.4              | 22.6                 |
| Smoky Tower                 | 71.6          | 81.5              | 18.5                 | 71.8                     | 81.3              | 18.7                 |
| Blackfoot (JM) <sup>1</sup> | 68.8          | 83.5              | 16.5                 | 69.4                     | 82.0              | 18.0                 |

<sup>1</sup> Blackfoot (Jerry mine).**Table 10.** Particle size effect in TGA micro-assay (g/100 g daf coal)

| Particle sizes | ASTM fixed carbon of coal | Volatile matter |       | Fixed carbon in char |            |
|----------------|---------------------------|-----------------|-------|----------------------|------------|
|                |                           | 400°C           | 550°C | 400°C char           | 550°C char |
| 100 micron     | 63.2                      | 10.6            | 25.9  | 70.3                 | 85.9       |
| 100-40 micron  | 64.3                      | 10.4            | 25.9  | 72.9                 | 85.6       |

**Table 11.** Pyrolysis (550°C) product distribution: calculated and experimental

| COAL   |              | Moisture ash-free weight percent distribution as |       |                 |                                |   |           |
|--|--------------|--|-------|-----------------|--------------------------------|---|-----------|
| Name/Unit formula  |              | Char   | Water | Oxide of carbon | C <sub>1</sub> -C <sub>6</sub> | NH <sub>3</sub> + H <sub>2</sub> S + H <sub>2</sub> | Oil + Tar |
| Smoky Tower  | calculated   | 71.6   | 9.1   | 1.5             | 0.6                            | 0.5   | 16.5      |
| C <sub>60</sub> H <sub>48</sub> N <sub>1.2</sub> S <sub>0.2</sub> O <sub>10</sub>  | experimental | 71.6   | 9.1   | -----           | 12.2-----                      | -----   | 7.1       |
| Fox Creek  | calculated   | 73.7   | 9.7   | 1.76            | 0.54                           | 0.4   | 13.7      |
| C <sub>93</sub> H <sub>62</sub> N <sub>1.2</sub> S <sub>0.2</sub> O <sub>17</sub>  | experimental | 74.7   | 9.7   | -----           | 10.3-----                      | -----   | 5.3       |
| Judy Creek   | calculated   | 73.6   | 8.7   | 4.2             | 0.9                            | 0.3   | 12.3      |
| C <sub>112</sub> H <sub>73</sub> N <sub>1.1</sub> S <sub>0.2</sub> O <sub>22</sub> | experimental | 74.6   | 8.7   | -----           | 11.6-----                      | -----   | 5.1       |
| Highvale   | calculated   | 74.7   | 9.8   | 1.3             | 0.4                            | 0.4   | 13.4      |
| C <sub>108</sub> H <sub>76</sub> N <sub>1.3</sub> S <sub>0.2</sub> O <sub>21</sub> | experimental | 74.5   | 9.8   | -----           | 12.7-----                      | -----   | 3.0       |
| Ardley   | calculated   | 76.0   | 10.3  | 1.8             | 0.4                            | 0.4   | 11.1      |
| C <sub>85</sub> H <sub>56</sub> N <sub>1.2</sub> S <sub>0.2</sub> O <sub>16</sub>  | experimental | 75.1   | 10.3  | -----           | 11.4-----                      | -----   | 3.2       |
| Vesta  | calculated   | 71.1   | 9.9   | 3.8             | 0.6                            | 0.3   | 14.2      |
| C <sub>61</sub> H <sub>48</sub> N <sub>1.1</sub> S <sub>0.2</sub> O <sub>16</sub>  | experimental | 69.6   | 9.9   | -----           | 15.3-----                      | -----   | 5.2       |
| Egg Lake   | calculated   | 71.0   | 10.9  | 3.4             | 0.6                            | 0.6   | 13.4      |
| C <sub>67</sub> H <sub>48</sub> N <sub>1.3</sub> S <sub>0.2</sub> O <sub>13</sub>  | experimental | 70.7   | 10.9  | -----           | 13.8-----                      | -----   | 4.6       |
| Blackfoot, Jerry mine  | calculated   | 68.9   | 9.5   | 9.4             | 0.9                            | 0.7   | 10.7      |
| C <sub>56</sub> H <sub>38</sub> N <sub>1.2</sub> S <sub>0.1</sub> O <sub>13</sub>  | experimental | 68.8   | 9.5   | -----           | 18.1-----                      | -----   | 3.6       |
| Blackfoot, west pit  | calculated   | 73.2   | 9.7   | 4.9             | 1.4                            | 0.5   | 10.3      |
| C <sub>49</sub> H <sub>34</sub> N <sub>1.1</sub> S <sub>0.1</sub> O <sub>9.5</sub> | experimental | 73.2   | 9.7   | -----           | 12.2-----                      | -----   | 4.9       |
| Bow City   | calculated   | 66.7   | 7.2   | 5.0             | 1.6                            | 0.5   | 18.9      |
| C <sub>49</sub> H <sub>42</sub> N <sub>1.02</sub> O <sub>7.8</sub>                 | experimental | 66.8   | 7.2   | -----           | 13.3-----                      | -----   | 12.7      |

Note: Experimental values: Fischer Assay results.

Calculated values: computed from elemental analyses of coal and char assuming volatile matter appeared in products as shown.



**Table 12.** Fischer gas analysis (percent volume)

| Coal                              | Bow City | Blackfoot<br>Jerry mine | Blackfoot<br>west pit | Highvale | Judy<br>Creek | Fox<br>Creek | Vesta | Smoky<br>Tower | Ardley | Egg<br>Lake |
|-----------------------------------|----------|-------------------------|-----------------------|----------|---------------|--------------|-------|----------------|--------|-------------|
| Gas composition                   |          |                         |                       |          |               |              |       |                |        |             |
| CO                                | 14.54    | 18.40                   | 21.40                 | 16.10    | 16.10         | 15.30        | 16.50 | 15.50          | 17.30  | 19.20       |
| CO <sub>2</sub>                   | 48.24    | 64.40                   | 44.50                 | 59.00    | 55.70         | 48.50        | 59.20 | 48.90          | 54.50  | 50.90       |
| H <sub>2</sub>                    | 5.72     | 3.10                    | 5.00                  | 5.50     | 5.70          | 7.20         | 4.30  | 5.70           | 4.20   | 5.20        |
| CH <sub>4</sub>                   | 21.00    | 10.70                   | 21.70                 | 15.10    | 17.20         | 21.70        | 14.50 | 20.60          | 17.50  | 18.50       |
| C <sub>2</sub> H <sub>6</sub>     | 2.06     | 0.80                    | 2.30                  | 1.23     | 1.33          | 2.03         | 1.28  | 2.10           | 1.84   | 2.18        |
| C <sub>2</sub> H <sub>4</sub>     | 1.69     | 0.23                    | 1.35                  | 1.23     | 0.53          | 1.43         | 0.48  | 1.50           | 1.34   | 0.85        |
| C <sub>3</sub> H <sub>8</sub>     | 1.90     | 0.73                    | 1.20                  | 0.94     | 1.01          | 1.31         | 1.06  | 1.60           | 1.10   | 1.00        |
| C <sub>3</sub> H <sub>6</sub>     | 1.51     | 0.56                    | 0.92                  | 0.70     | 0.96          | 1.09         | 1.90  | 1.22           | 0.99   | 0.85        |
| C <sub>4</sub> H <sub>10-n</sub>  | 0.39     | 0.10                    | 0.18                  | 0.13     | 0.14          | 0.18         | 0.16  | 0.26           | 0.15   | 0.15        |
| C <sub>4</sub> H <sub>10-i</sub>  | 0.07     | 0.03                    | 0.05                  | 0.04     | 0.04          | 0.05         | 0.03  | 0.08           | 0.06   | 0.05        |
| C <sub>4</sub> H <sub>8</sub> *   | 0.64     | 0.11                    | 0.36                  | 0.46     | 0.61          | 0.74         | 0.60  | 0.81           | 0.62   | 0.52        |
| C <sub>6</sub> H <sub>12</sub> ** | 0.20     | 0.04                    | 0.23                  | 0.04     | 0.04          | 0.19         | 0.10  | 0.23           | 0.17   | 0.14        |
| H <sub>2</sub> S                  | 0.89     | 0.35                    | 0.84                  | 0.24     | 0.68          | 0.72         | 0.59  | 0.41           | 0.50   | 0.46        |
| COS                               | 0.02     | 0.01                    | 0.03                  | —        | 0.02          | 0.02         | 0.01  | 0.01           | —      | 0.01        |

\*\* two isomer (1 and 2)

\* various isomers

**Table 13.** Proximate and elemental analysis of 550°C Fischer char (g/100 g daf char)

| Sample specification   |        | Volatile<br>matter | Fixed<br>carbon | Carbon | Hydrogen | Nitrogen | Sulfur | Oxygen |
|------------------------|--------|--------------------|-----------------|--------|----------|----------|--------|--------|
| Name                   | Number |                    |                 |        |          |          |        |        |
| Smoky Tower            | 1      | 18.5               | 81.5            | 83.8   | 2.93     | 2.08     | 0.50   | 10.7   |
| Fox Creek              | 2      | 18.8               | 81.2            | 84.0   | 2.81     | 1.29     | 0.42   | 11.5   |
| Judy Creek             | 3      | 19.3               | 80.7            | 83.7   | 2.85     | 1.07     | 0.39   | 12.0   |
| Highvale               | 5      | 20.4               | 79.6            | 83.0   | 2.80     | 1.10     | 0.17   | 12.9   |
| Ardley                 | 7      | 19.3               | 80.7            | 84.6   | 2.92     | 1.35     | 0.35   | 10.8   |
| Blackfoot (Jerry mine) | 10a    | 16.6               | 83.4            | 84.2   | 2.73     | 2.18     | 0.36   | 10.5   |
| Blackfoot (west pit)   | 10b    | 16.9               | 83.1            | 84.6   | 3.03     | 2.42     | 0.35   | 9.6    |
| Egg Lake               | 4      | 18.6               | 81.4            | 84.7   | 2.89     | 1.82     | 0.31   | 10.3   |
| Vesta                  | 8      | 17.9               | 82.1            | 84.8   | 2.92     | 2.02     | 0.50   | 9.8    |
| Bow City               | 11     | 17.8               | 82.2            | 84.3   | 3.10     | 2.71     | 0.75   | 9.20   |

Note: All analyses are weight percentage of moisture ash-free char.

**Table 14.** Conversion values for liquefaction processes (g/100 g daf coal)

| Coal name    | Process name |            |           |            |           |         |
|--------------|--------------|------------|-----------|------------|-----------|---------|
|              | PC-1         | PC-2       | PC-3      | PC-4-1     | PC-4-2    | Average |
| Smoky Tower  | 80.5(4.9)    | 88.6(4.5)  | 92.5(0.7) | 84.0(2.8)  | 84.6(8.0) | 86      |
| Fox Creek    | 77.5(5.5)    | 85.5(7.8)  | 89.0(0.0) | 84.0(1.4)  | 87.0(1.4) | 85      |
| Judy Creek   | 75.6(5.3)    | 91.0(5.0)  | 86.5(2.5) | 82.5(2.1)  | 85.5(0.7) | 84      |
| Highvale     | 62.7(8.3)    | 76.3(12.1) | 83.6(7.4) | 83.0(2.8)  | 84.0(1.7) | 78      |
| Ardley       | 77.8(3.2)    | 76.7(7.9)  | 86.1(1.3) | 68.3(15.3) | 81.0(1.4) | 78      |
| Egg Lake     | 87.0(4.2)    | 95.3(0.6)  | 95.5(0.7) | 93.7(1.2)  | 93.7(0.3) | 93      |
| Vesta        | 92.5(3.0)    | 94.9(0.9)  | 95.5(0.7) | 94.8(3.9)  | 96.5(0.7) | 95      |
| Battle River | 91.0(1.4)    | 93.5(0.7)  | 94.5(0.7) | 92.5(0.7)  | 95.3(0.6) | 93      |

Note: Numbers in parenthesis are standard deviations between replicate runs. Average SD of the entire population pool of 178 runs is 3.0.

**Table 15.** Liquid yields from liquefaction processes (percent weight of input solvent)

| Coal name    | Process name |      |      |        |        |         |
|--------------|--------------|------|------|--------|--------|---------|
|              | PC-1         | PC-2 | PC-3 | PC-4-1 | PC-4-2 | Average |
| Smoky Tower  | 124          | 127  | 129  | 120    | 121    | 124     |
| Fox Creek    | 123          | 130  | 127  | 119    | 124    | 124     |
| Judy Creek   | 121          | 130  | 121  | 120    | 121    | 123     |
| Highvale     | 116          | 123  | 126  | 115    | 123    | 120     |
| Ardley       | 125          | 124  | 127  | 112    | 124    | 122     |
| Egg Lake     | 131          | 129  | 130  | 123    | 124    | 127     |
| Vesta        | 129          | 129  | 130  | 127    | 129    | 129     |
| Battle River | 127          | 131  | 130  | 121    | 120    | 126     |

Note: The coal input in each run was 50 grams (moisture ash-free).

**Table 16.** Net liquid yields based on blank run normalization (g/100 g daf coal)

| Coal samples                            | Process        |                |                     |                     |
|---|----------------|----------------|---------------------|---------------------|
|   | PC-3           | PC-4-1         | PC-2                | PC-4-2              |
| Coals 2, 3, 5 and 7<br>(Group average)  | 50.5           | 34.8           | 54.0                | 47.2                |
| Coal 1                                  | 59.0           | 40.0           | 55.0                | 42.0                |
| Coals 4, 6, 8 and 8a<br>(Group average) | 61.5           | 48.2           | 60.0                | 48.4                |
| Solvent                                 | Anthracene oil | Bitumen        | Anthracene oil      | Bitumen             |
| Reducing gas                            | H <sub>2</sub> | H <sub>2</sub> | CO/H <sub>2</sub> O | CO/H <sub>2</sub> O |

Note: Results computed from data of optimum conversions normalized on the basis of blank runs without coal.



**Table 17.** Computed versus experimental volatile matter content of the test coalsAssumption: ASTM fixed carbon composition:  $\text{CH}_{0.22}\text{N}_{0.01}\text{S}_{0.002}\text{O}_{0.02}$ 

| Coal Name                 | Volatile yields, g/100 g daf coal |          |                           |          |                 |          |               |            |      |
|---------------------------|-----------------------------------|----------|---------------------------|----------|-----------------|----------|---------------|------------|------|
|                           | Fischer assay                     |          | Volatile left in 550 Char |          | Total volatiles |          | ASTM volatile | Difference |      |
|                           | Experimental                      | Computed | Experimental              | Computed | Experimental    | Computed | Experimental  | 1          | 2    |
| Smoky Tower               | 28.4                              | 28.4     | 13.2                      | 12.5     | 41.6            | 40.9     | 43.4          | -1.8       | -2.5 |
| Fox Creek                 | 25.3                              | 26.3     | 14.0                      | 13.1     | 39.3            | 39.4     | 40.0          | -0.7       | -0.6 |
| Judy Creek                | 25.4                              | 26.4     | 14.4                      | 13.6     | 39.8            | 40.0     | 40.5          | -0.7       | -0.5 |
| Highvale                  | 25.5                              | 25.3     | 15.2                      | 15.1     | 40.7            | 40.4     | 39.6          | +1.1       | +0.8 |
| Ardley                    | 24.9                              | 24.0     | 14.5                      | 12.6     | 39.4            | 36.6     | 39.3          | +0.1       | -2.7 |
| Vesta                     | 30.4                              | 28.9     | 12.5                      | 11.0     | 42.8            | 39.9     | 41.9          | +0.9       | -2.0 |
| Egg Lake                  | 29.3                              | 29.0     | 13.2                      | 11.5     | 42.5            | 40.5     | 43.2          | -0.7       | -2.7 |
| Blackfoot JM <sup>3</sup> | 31.2                              | 31.1     | 11.4                      | 11.7     | 42.6            | 42.8     | 44.2          | -1.6       | -1.4 |
| Blackfoot WP <sup>4</sup> | 26.8                              | 26.8     | 12.4                      | 11.6     | 39.2            | 38.4     | 41.3          | -2.1       | -2.9 |
| Bow City                  | 33.2                              | 33.3     | 11.9                      | 10.3     | 45.1            | 43.6     | 47.2          | -2.2       | -3.6 |

<sup>1</sup> difference between experimental values of two-stage pyrolysis (Coal 550 + char 950) and one stage (Coal 950).<sup>2</sup> as above but computed values from structural model and reaction model.<sup>3</sup> Blackfoot (Jerry mine).<sup>4</sup> Blackfoot (west pit).**Table 18.** Percentage of coal-oxygen removed as CO, CO<sub>2</sub>, H<sub>2</sub>O and liquefaction conversion

| Coal no. | Deoxygenation |                 | Liquefaction conversion<br>(daf coal wt) to soluble<br>and gaseous products |
|----------|---------------|-----------------|---|
|          | in pyrolysis  | in liquefaction |   |
| 1        | 56.8 ± 0.7    | 83.5 ± 12.2     | 85.5 ± 5.1  |
| 2        | 63.0 ± 0.2    | 80.2 ± 7.2      | 84.0 ± 5.8  |
| 3        | 76.4 ± 2.0    | 83.5 ± 4.0      | 84.0 ± 2.5  |
| 5        | 61.6 ± 2.2    | 89.4 ± 7.5      | 78.0 ± 8.1  |
| 7        | 56.5 ± 0.8    | 77.1 ± 9.7      | 78.0 ± 4.8  |
| 8        | 59.5 ± 1.0    | 83.9 ± 6.8      | 95.0 ± 2.5  |

**Table 19.** Computed potential hydrocarbon source matter (g/100 g daf coal)

| Test coal | PC-1 | PC-2 | PC-3 | PC-4-1 | PC-4-2 | Average        |         |
|-----------|------|------|------|--------|--------|----------------|---------|
|           |      |      |      |        |        | Anthracene oil | Bitumen |
| Coal 1    | 61   | 79   | 69   | 62     | 73     | 69.7           | 67.5    |
| Coal 2    | 61   | 71   | 73   | 64     | 73     | 68.3           | 68.5    |
| Coal 3    | 56   | 59   | 67   | 61     | 66     | 60.7           | 63.5    |
| Coal 5    | 49   | 71   | 70   | 59     | 70     | 63.3           | 64.5    |
| Coal 7    | 59   | 70   | 71   | 55     | 69     | 66.7           | 62.0    |
| Coal 8    | 77   | 83   | 77   | 74     | 83     | 79.0           | 78.5    |
| Average   | 60.5 | 72.2 | 71.2 | 62.5   | 72.3   | 68.0           | 67.4    |

**Table 20.** Computed yield of distillable products (g/125 g solvent + 50 g daf coal)

| Test sample    | PC-1       | PC-2      | PC-3       | PC-4-1    | PC-4-2    | Average |
|----------------|------------|-----------|------------|-----------|-----------|---------|
| Anthracene oil | 88.5(2.8)  | 94.3(4.0) | 91.7(2.1)  | —         | —         | —       |
| Bitumen        |            |           |            | 57.2(1.4) | 63.8(0.5) | 79.1    |
| Coal 1         | 93.4(2.0)  | 95.1(5.3) | 98.8(3.3)  | 65.8(0.6) | 63.2(3.5) | 84.2    |
| Coal 2         | 92.1(1.3)  | 66.1(5.6) | 81.8(3.5)  | 55.6(3.1) | 65.0(4.5) | 72.1    |
| Coal 3         | 90.6(7.7)  | 96.1(2.7) | 93.4(3.5)  | 60.2(4.7) | 50.8(3.7) | 78.2    |
| Coal 5         | 98.6(5.4)  | 96.0(3.7) | 96.2(4.5)  | 63.8(0.8) | 69.2(2.5) | 84.8    |
| Coal 7         | 92.8(2.8)  | 90.2(3.1) | 94.2(1.3)  | 67.1(0.5) | 64.5(0.4) | 81.8    |
| Coal 8         | 100.5(2.1) | 95.3(3.1) | 103.2(2.8) | 68.7(0.1) | 67.5(2.8) | 87.0    |
| Average        | 94.7       | 89.8      | 94.6       | 63.5      | 64.2      |         |

Note: Parenthetical references denote standard deviation.

**Table 21.** Computed yield of nondistillable products (g/125 g solvent + 50 g daf coal)

| Test sample    | PC-1      | PC-2      | PC-3      | PC-4-1    | PC-4-2    | Average |
|----------------|-----------|-----------|-----------|-----------|-----------|---------|
| Anthracene oil | 36.5(3.3) | 30.3(4.4) | 31.7(2.1) | —         | —         | —       |
| Bitumen        | —         | —         | —         | 60.6(2.4) | 47.0(0.8) | 41.2    |
| Coal 1         | 60.8(3.2) | 61.0(0.8) | 60.2(0.4) | 81.8(0.7) | 81.6(9.1) | 69.0    |
| Coal 2         | 59.7(3.0) | 94.6(8.6) | 73.6(6.0) | 89.7(3.6) | 86.2(4.1) | 80.8    |
| Coal 3         | 57.7(3.3) | 63.3(4.4) | 66.6(5.7) | 92.0(1.8) | 98.7(8.5) | 75.7    |
| Coal 5         | 47.4(5.2) | 58.9(2.4) | 61.2(9.8) | 78.3(1.7) | 82.0(6.0) | 65.6    |
| Coal 7         | 60.7(2.5) | 62.6(8.3) | 71.8(1.2) | 76.2(0.5) | 87.3(2.3) | 71.7    |
| Coal 8         | 58.5(3.3) | 59.3(5.2) | 56.3(2.2) | 86.9(1.8) | 91.0(4.2) | 70.4    |
| Average        | 56.5      | 66.6      | 65.0      | 84.2      | 82.8      |         |

Note: Parenthetical references denote standard deviation.

**Table 22.** Computed soluble product yield<sup>1</sup> (g/100 g daf coal)

| Test sample | PC-1 | PC-2  | PC-3  | PC-4-1 | PC-4-2 | Average        |         |
|-------------|------|-------|-------|--------|--------|----------------|---------|
|             |      |       |       |        |        | Anthracene oil | Bitumen |
| Coal 1      | 126  | 118   | 146   | 160    | 180    | 130            | 170     |
| Coal 2      | 133  | 189   | 148   | 178    | 172    | 156            | 175     |
| Coal 3      | 119  | 156   | 133   | 160    | 196    | 136            | 178     |
| Coal 5      | 95   | 116   | 145   | 155    | 148    | 118            | 152     |
| Coal 7      | 118  | 130   | 140   | 151    | 178    | 129            | 164     |
| Coal 8      | 141  | 142   | 136   | 164    | 164    | 143            | 164     |
| Average     | 122  | 143.5 | 141.3 | 161.3  | 173.0  |                |         |

<sup>1</sup> distillable product plus extract from output slurry.



**Table 23.** Extract to PHS ratio (see tables 19 and 22)

| Test sample | PC-1 | PC-2 | PC-3 | PC-4-1 | PC-4-2 | Average        |         |
|-------------|------|------|------|--------|--------|----------------|---------|
|             |      |      |      |        |        | Anthracene oil | Bitumen |
| Coal 1      | 2.06 | 1.49 | 2.11 | 2.58   | 2.46   | 1.87           | 2.52    |
| Coal 2      | 2.18 | 2.66 | 2.03 | 2.78   | 2.66   | 2.29           | 2.72    |
| Coal 3      | 2.12 | 2.64 | 1.99 | 2.62   | 2.92   | 2.25           | 2.80    |
| Coal 5      | 1.94 | 1.63 | 2.07 | 2.25   | 2.11   | 1.88           | 2.18    |
| Coal 7      | 2.00 | 1.85 | 1.97 | 2.74   | 2.58   | 1.94           | 2.66    |
| Coal 8      | 1.83 | 1.83 | 1.77 | 2.22   | 1.98   | 1.81           | 2.10    |
| Average     | 2.02 | 2.02 | 1.99 | 2.53   | 2.46   | 2.01           | 2.50    |

**Table 24.** Comparison of Japanese and Alberta Research Council results (g/100 g daf coal)

| Coal    | Conversion |                  | Oil yield |                  |
|---------|------------|------------------|-----------|------------------|
|         | Japan      | Research Council | Japan     | Research Council |
| Coal 5  | 87         | 78               | 53        | 43               |
| Coal 7  | 81         | 78               | 61        | 50               |
| Coal 1  | 92         | 86               | 65        | 59               |
| Vesta 8 | 100        | 95               | 70        | 59               |

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## Appendix A

### Comparative pyrolysis characteristics of other Canadian coals of cretaceous and carboniferous deposits<sup>1</sup>

Fischer assay (535°C) report of 12 Canadian coals from east and west provinces is given below. The coals were analyzed by NMR techniques. Carbon-13 NMR spectra were obtained at 45.28 MHz on a Bruker CXP-180 NMR spectrometer by means of cross-polarization dipolar decoupling and magic angle sample spinning techniques. A single matched 1-ms cross-polarization contact was used with radio-frequency field amplitudes of 45kHz. The delay time between successive contacts was 2s. Spin-temperature alternation was used as well as flip-back of the proton magnetization

after data acquisition. The adjustment of the Hartmann-Hahn matching condition was checked during the course of the experiments by inserting a standard hexamethyl benzene sample in the probe. A sweep width setting of 20 kHz was employed to acquire 500 pt free induction decays, which was zero filled to 4K before Fourier transformation. Magic angle spinning was performed at 3.4 kHz with Kel-F rotors of the Andrew type. Intensities of the aliphatic and aromatic bands were corrected for spinning side bands, assuming the first order high and low field sides and intensities to be the same.

<sup>1</sup> — Adapted from E. Furlmsky, L. Vancea and R. Belanger (1984): Effect of coal rank on structure of tars from low-temperature pyrolysis of Canadian coals; Industrial Engineering Chemistry, Product Research and Development, vol. 23, pp. 134-140.

### Pyrolysis results (Fischer assay)

| Coal Specimen    | Dry ash | Rank <sup>a</sup> | Mean             | Volatile <sup>b</sup> | Aromaticity                         | Composition <sup>c</sup> |          |        |        | Pyrolysis results <sup>b</sup> |      |       |
|------------------|---------|-------------------|------------------|-----------------------|-------------------------------------|--------------------------|----------|--------|--------|--------------------------------|------|-------|
|                  |         | % C               | % R <sub>O</sub> | matter                | C <sub>ar</sub> /C <sub>total</sub> | Hydrogen                 | Nitrogen | Sulfur | Oxygen | Char                           | Tar  | Water |
| British Columbia |         |                   |                  |                       |                                     |                          |          |        |        |                                |      |       |
| Balmer           | 11.6    | 90.1              | 1.38             | 22.7                  | 0.80                                | 65.3                     | 1.60     | 0.09   | 2.53   | 87.9                           | 6.4  | 1.35  |
| Sukumka          | 3.4     | 88.5              | 1.41             | 25.3                  | 0.79                                | 66.6                     | 1.32     | 0.22   | 3.93   | 87.4                           | 5.2  | 1.05  |
| Byron Creek      | 22.3    | 85.7              | 0.93             | 22.3                  | 0.74                                | 68.0                     | 1.29     | 0.17   | 6.76   | 83.2                           | 9.0  | 1.29  |
| Alberta          |         |                   |                  |                       |                                     |                          |          |        |        |                                |      |       |
| Canmore          | 9.5     | 91.4              | 2.12             | 14.1                  | 0.86                                | 53.2                     | 1.70     | 0.40   | 1.50   | 95.7                           | 0.8  | 0.57  |
| McIntyre         | 8.4     | 90.5              | 1.49             | 20.7                  | 0.77                                | 61.6                     | 1.27     | 0.28   | 2.31   | 90.0                           | 3.7  | 0.89  |
| Coalspur         | 10.5    | 79.5              | 0.57             | 40.9                  | 0.67                                | 75.8                     | 1.33     | 0.12   | 13.20  | 75.6                           | 10.4 | 6.42  |
| Shaughnessy      | 12.5    | 76.1              | 0.50             | 43.6                  | 0.65                                | 84.7                     | 2.18     | 0.44   | 15.36  | 73.1                           | 12.1 | 5.80  |
| E. Blackfoot     | 33.4    | 70.8              | 0.49             | 52.5                  | 0.58                                | 98.1                     | 1.91     | 0.25   | 22.55  | 68.6                           | 5.0  | 10.10 |
| Manitoba         |         |                   |                  |                       |                                     |                          |          |        |        |                                |      |       |
| Bienfait         | 11.3    | 72.8              | 0.40             | 48.5                  | 0.57                                | 79.4                     | 1.52     | 0.42   | 20.83  | 65.3                           | 4.7  | 11.0  |
| Ontario          |         |                   |                  |                       |                                     |                          |          |        |        |                                |      |       |
| Onacawana        | 36.6    | 67.8              | 0.25             | 54.5                  | 0.57                                | 81.0                     | 1.23     | 4.08   | 21.10  | 63.9                           | 4.2  | 12.0  |
| Nova Scotia      |         |                   |                  |                       |                                     |                          |          |        |        |                                |      |       |
| Devco            | 2.8     | 87.3              | 0.93             | 38.6                  | 0.69                                | 82.9                     | 1.85     | 0.77   | 4.77   | 73.9                           | 14.2 | 4.2   |
| Prince           | 18.6    | 80.6              | 0.67             | 43.0                  | 0.71                                | 82.4                     | 1.75     | 2.89   | 5.54   | 72.4                           | 12.5 | 5.8   |

a. based on moisture ash-free carbon

b. weight percentage of moisture, ash-free coal

c. given as atoms per 100 carbon atoms

## Appendix B

### Comparative liquefaction characteristics of Alberta mountain and foothills coals<sup>1</sup>

Hydroliquefaction of twelve coals from Kootenay and Belly River horizons was performed using tetralin as solvent and molybdenum oxide as catalyst impregnated on coal. The reactions were conducted in batch autoclave at 425-450°C and 2600 psi hydrogen pressure for eight hours. The oily mass from the autoclave was filtered by suction and the residual solids washed with ether and subsequently dried and weighed to measure net conversion. The combined oils were subjected to

distillation. The final fraction, distilling up to 300°C, was recorded as distillable oil. The residue was a stable pitch boiling at temperature as high as 450°C without decomposition. There was a considerable loss of tetralin. The coal analyses along with the results of liquefaction reactions are as follows:

<sup>1</sup> — From E.H. Boomer, A.W. Saddington and J. Edwards (1935): The hydrogenation of Alberta coals; II, Comparative data on thirteen coals of various ranks and two suspension media, tetralin and liquid petrolatum, Canadian Journal of Research, vol. 13, section B, pp. 11-27.

## Liquefaction results

| Coal specimen | Dry ash | Rank <sup>a</sup><br>% C | Composition <sup>b</sup> |          |        |        | Liquefaction results <sup>c</sup> |                    |       |       |
|---------------|---------|--------------------------|--------------------------|----------|--------|--------|-----------------------------------|--------------------|-------|-------|
|               |         |                          | Hydrogen                 | Nitrogen | Sulfur | Oxygen | Conversion                        | Liquid<br>bp-300°C | Pitch | Water |
| Canmore       | 6.0     | 90.7                     | 57.4                     | 1.60     | 0.33   | 2.07   | 35                                | —                  | 17    | 0.6   |
| Coleman       | 7.3     | 88.3                     | 69.4                     | 1.26     | 0.19   | 4.08   | 72                                | 4                  | 44    | 0.8   |
| Bellevue      | 15.1    | 87.3                     | 76.4                     | 1.47     | 0.19   | 4.47   | 85                                | 20                 | 40    | 3.0   |
| Pincher Creek | 10.1    | 84.7                     | 74.2                     | 1.21     | 0.21   | 7.40   | 87                                | 20                 | 40    | 3.0   |
| Lundbreck     | 13.9    | 83.3                     | 74.1                     | 2.37     | 0.27   | 7.77   | 92                                | 37                 | 27    | 12.2  |
| Lethbridge    | 10.8    | 79.1                     | 80.6                     | 2.06     | 0.26   | 12.46  | 91                                | 22                 | 31    | 11.2  |
| Champion      | 7.7     | 78.6                     | 80.3                     | 1.42     | 0.17   | 13.74  | 89                                | 25                 | 25    | 10.2  |
| Taber         | 8.8     | 77.4                     | 79.3                     | 2.21     | 0.32   | 14.35  | 95                                | 27                 | 28    | 8.1   |
| Grassy Lake   | 10.6    | 76.7                     | 79.2                     | 2.12     | 0.44   | 15.07  | 96                                | 30                 | 21    | 16.0  |
| Winnifred     | 10.0    | 74.9                     | 77.8                     | 1.60     | 0.35   | 18.15  | 91                                | 25                 | 23    | 17.0  |
| Redcliff      | 10.4    | 73.1                     | 79.1                     | 1.29     | 0.28   | 20.95  | 97                                | 33                 | 24    | 19.0  |
| Eagle Butte   | 12.2    | 71.7                     | 74.8                     | 1.32     | 0.21   | 23.41  | 96                                | 33                 | 19    | 17.0  |

a. based on moisture, ash-free coal carbon

b. given as atoms per 100 carbon atoms

c. weight percentages of moisture, ash-free coal

## Appendix C

### Definition of some special terms

*assumed molecular size of coal* is the formula weight of an average coal molecule derived empirically from the elemental composition of coal and its 550°C char containing one nitrogen atom.

*aromaticity* is a computed number denoting the fraction of coal carbon retained in 850°C char or coke assuming that aromatic C-H, C-N and C-O functions are preserved in the fixed carbon.

*effective volatile content* is a measure of potential liquid and gas yields from a given coal subjected to any pyrolysis process.

*oxidation state of volatile carbon structure*  $f_{CH}$ , is an empirically defined chemical property related to the elemental compositions and the valence states of the elements present as thermally unstable structures in coal. Relative values of  $f_{CH}$

give a comparison between coals on the basis of the oxygen contents of the volatile matter given off at a selective temperature of pyrolysis.

*organic part* is the moisture, ash-free (daf) portion of coal particle or coal-derived solid matter after pyrolytic or other types of coal processing.

*potential hydrocarbon source matter*, PHS, is a part of coaly matter soluble in organic solvent, generated under selective solvolytic conditions, which can be upgraded to a mixture of hydrocarbons. In the text, PHS values for Alberta plains coals are calculated as equal to (100 - CO - CO<sub>2</sub> - H<sub>2</sub>O - Insoluble organic matter) weight percentage of moisture ash-free coal from selective solvolytic reactions producing solid, liquid, extractable fluids and gaseous products by interacting with solvent.





N.L.C. - B.N.C.



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